

From the INTERNATIONAL BUREAU

## PCT

### NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE  
in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 13 July 2001 (13.07.01)	
<b>International application No.</b> PCT/US00/23911	<b>Applicant's or agent's file reference</b> 3041-022
<b>International filing date (day/month/year)</b> 01 September 2000 (01.09.00)	<b>Priority date (day/month/year)</b> 03 September 1999 (03.09.99)
<b>Applicant</b> KRAFTON, Brian, D. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
03 April 2001 (03.04.01)

☐ in a notice effecting later election filed with the International Bureau on:  
\_\_\_\_\_

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b>  <p style="text-align: center;">Nestor Santesso</p> Telephone No.: (41-22) 338.83.38
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**PCT**  
**DEMAND**

**CHAPTER II**

under Article 31 of the Patent Cooperation Treaty:  
The undersigned requests that the international application specified below be the subject of  
international preliminary examination according to the Patent Cooperation Treaty.

For International Preliminary Examining Authority use only

Identification of IPEA

Date of receipt of DEMAND

**Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION**

Applicant's or agent's file reference  
3041-22

International application No.

PCT/US00/23911

International filing date (day/month/year)

01/09/00

(Earliest) Priority date (day/month/year)

03/09/99

Title of invention

**A GENERATOR FOR GENERATING CHLORINE DIOXIDE UNDER VACUUM EDUCTION IN A SINGLE PASS**

**Box No. II APPLICANT(S)**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

INTERNATIONAL DIOXIDE, INC.  
554 Ten Rod Road  
North Kingston, Rhode Island 02852  
United States of America

Telephone No.:

Facsimile No.:

Teleprinter No.:

State (i.e. country) of nationality: US

State (i.e. country) of residence: US

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

KRAFTON, BRIAN D.  
25 Paddock Court  
Wakefield, RI 02879  
United States of America

State (i.e. country) of nationality: US

State (i.e. country) of residence: US

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

SMEDLEY, JOHN C.  
5707 N.W. Oakridge Court  
Platte Woods, MO 64151  
United States of America

State (i.e. country) of nationality: US

State (i.e. country) of residence: US

☒ Further applicants are indicated on a continuation sheet.

Continuation of Box No. II APPLICANT(S)

*If none of the following sub-boxes is used, this sheet should not be included in the demand.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

KUCHER, DONALD C.  
1520 Oak Lane  
Quackertown, PA 18951  
United States of America

State (i.e. country) of nationality: US

State (i.e. country) of residence: US

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

State (i.e. country) of nationality:

State (i.e. country) of residence:

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

State (i.e. country) of nationality:

State (i.e. country) of residence:

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

State (i.e. country) of nationality:

State (i.e. country) of residence:

Further applicants are indicated on a continuation sheet.

**Box No. III AGENT OR COMMON REPRESENTATIVE, OR ADDRESS FOR CORRESPONDENCE**

The following person is ☒ agent ☐ common representative

and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.

☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. the address must include postal code and name of country.)*

KELLEY, MARGARET B.  
Clifford Chance Rogers & Wells LLP  
200 Park Avenue  
New York, NY 10166  
United States of America

Telephone No.:  
212-878-3145

Facsimile No.:  
212-878-8375

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:\***

1. The applicant wishes the International Preliminary examining Authority\*

☒ the international application as originally filed

the description ☒ as originally filed

☐ as amended under Article 34

the claims ☐ as originally filed

☐ as amended under Article 19 (together with any accompanying statement)

☒ as amended under Article 34

the drawings ☒ as originally filed

☐ as amended under Article 34

2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This checkbox may be marked only where the time limit under Article 19 has not yet expired)*

\* Where no check-box is marked, International preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international of international preliminary examination: English.....

☒ which is the language in which the international application was filed.

☐ which is the language of a translation furnished for the purposes of international search.

☐ which is the language of publication of the international application.

☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

**Box No. V ELECTION OF STATES**

The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)* excluding the following States which the applicant wishes not to elect:

Box No. VI CHECKLIST

The demand is accompanied by the following elements in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- |    |   |   |                 |
|----|---|---|-----------------|
| 1. | translation of international application                              | : | _____ sheets    |
| 2. | amendments under Article 34   | : | _____ sheets    |
| 3. | copy (or, where required, translation) of amendments under Article 19 | : | _____ sheets    |
| 4. | copy (or, where required, translation) of statement under Article 19  | : | _____ sheets    |
| 5. | letter:   | : | <u>4</u> sheets |
| 6. | other (specify) <i>Certificate of Express Mail</i>                    | : | <u>1</u> sheets |

For International Preliminary Examining Authority use only

Received

Not Received

<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- |    |   |
|----|---|
| 1. | <input checked="" type="checkbox"/> fee calculation sheet                             |
| 2. | <input type="checkbox"/> separate signed power of attorney                            |
| 3. | <input type="checkbox"/> copy of general power of attorney: reference number, if any: |

- |    |   |
|----|---|
| 4. | <input type="checkbox"/> statement explaining lack of signature   |
| 5. | <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form                      |
| 6. | <input checked="" type="checkbox"/> other (specify) <i>Certificate of Express Mailing and Return-Receipt Postcard</i> |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

*Margaret B. Kelley*  
Margaret B. Kelley, Esq.  
Reg. No. 29,181

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND \_\_\_\_\_

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been Informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

Demand received from IPEA on:

For International Bureau use only

# FEE CALCULATION SHEET

Annex to Demand for international preliminary examination

International application No. PCT/US00/23911		For International Preliminary Examining Authority use only	
Applicant's or agent's file reference 3041-22		Date stamp of the IPEA	
Applicant: INTERNATIONAL DIOXIDE, INC...			
<b>Calculation of prescribed fees</b>			
1. Preliminary examination fee .....	490.00	P	
2. Handling fee (Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)	137.00	H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL Box.....	\$627.00		
	Total		
<b>Mode of Payment</b>			
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> authorization to charge deposit account with the IPEA (see below)           </div> <div> <input type="checkbox"/> cash           </div> </div>			
<div style="display: flex; justify-content: space-between;"> <div> <input type="checkbox"/> cheque           </div> <div> <input type="checkbox"/> revenue stamps           </div> </div>			
<div style="display: flex; justify-content: space-between;"> <div> <input type="checkbox"/> postal money order           </div> <div> <input type="checkbox"/> coupons           </div> </div>			
<div style="display: flex; justify-content: space-between;"> <div> <input type="checkbox"/> bank draft           </div> <div> <input type="checkbox"/> other (specify):           </div> </div>			
<b>Deposit Account Authorization</b> (this mode of payment may not be available at all IPEAs)			
The IPEA/US <input checked="" type="checkbox"/> is hereby authorized to charge the total fees indicated above to my deposit account.			
<input checked="" type="checkbox"/> (this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.			
50-0521 Deposit Account Number		<div style="display: flex; justify-content: space-between;"> <div>           Date <u>April 3, 2001</u> (day/month/year)         </div> <div>           Signature <u>Margaret B. Kelly</u> </div> </div>	

10/070,052

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

6  
18 APR 2002

Applicant's or agent's file reference 3041-022		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/23911	International filing date (day/month/year) 01 SEPTEMBER 2000	Priority date (day/month/year) 03 SEPTEMBER 1999	
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.			
Applicant INTERNATIONAL			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets.


☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

CORRECTED VERSION

Date of submission of the demand 03 APRIL 2001	Date of completion of this report 01 FEBRUARY 2002
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer DONALD R. VALENTINE 
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

## I. Basis of the report

1. With regard to the elements of the international application:\*

☐ the international application as originally filed

☒ the description:

pages (See Attached)

pages , as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the claims:

pages (See Attached)

pages , as originally filed

pages , as amended (together with any statement) under Article 19

pages , filed with the demand

pages , filed with the letter of

☒ the drawings:

pages (See Attached)

pages , as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the sequence listing part of the description:

pages (See Attached)

pages , as originally filed

pages , filed with the demand

pages , filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. NONE

☒ the drawings, sheets/fig NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. statement

Novelty (N)

Claims 1-35

YES

Claims NONE

NO

Inventive Step (IS)

Claims 1-35

YES

Claims NONE

NO

Industrial Applicability (IA)

Claims 1-35

YES

Claims NONE

NO

### 2. citations and explanations (Rule 70.7)

Claims 1-35 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest an electrolytic generator for generating chlorine dioxide which comprises, in combination, a high surface area porous anode; corrosion resistant cathode; cation ion exchange membrane separating anode and cathode into anode and cathode compartments; an array of non-corrosive support ribbing for the membrane; catholyte and anolyte cell frames with inlets and outlets; anolyte infeed means; inlet means for softened, deionized or demineralized purge water including a line with a solenoid followed by a rotameter and a flow switch; catholyte infeed means; ascending anolyte outfeed means; an eductor connected to the anolyte infeed means; motive water infeed means; catholyte outfeed means; sensor connected to the anolyte outfeed means prior to the eductor; pressure switch on the motive infeed means; and D.C. power supply and automatic current interrupter for preventing reverse current flow across the cell upon shutdown. Further, the prior art does not show or suggest a method for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor which comprises feeding buffered aqueous alkali metal solution to the anolyte compartment of an electrolytic generator, feeding water to the generator catholyte compartment, supplying motive inert gas to an eductor to create a vacuum in the anolyte compartment and recovering the mist from the anolyte compartment.

Claims 1-35 meet the criteria set out in PCT Article 33(4), because the invention has industrial applicability in the area of disinfecting food stuffs, fields, greenhouses, storage cellars, and autoclaves.

NEW CITATIONS  
(Continued on Supplemental Sheet.)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:  
IPC(7): A01N 2/08, 25/06; C25B 1/24, 9/00, 11/00, 11/04, 11/12, 15/00 and US Cl.: 204/230.3, 230.5, 265, 266, 284, 290.12, 290.14, 291, 292, 293, 294; 205/556, 701; 422/28; 424/40

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,  
page(s) 1-22, as originally filed.  
page(s) NONE, filed with the demand.  
and additional amendments:  
NONE

This report has been drawn on the basis of the claims,  
page(s) 23-26, as originally filed.  
page(s) NONE, as amended under Article 19.  
page(s) NONE, filed with the demand.  
and additional amendments:  
Page 27, file with the letter of 20 November 2001.

This report has been drawn on the basis of the drawings,  
page(s) 1-9, as originally filed.  
page(s) NONE, filed with the demand.  
and additional amendments:  
NONE

This report has been drawn on the basis of the sequence listing part of the description:  
page(s) NONE, as originally filed.  
pages(s) NONE, filed with the demand.  
and additional amendments:  
NONE

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):  
US 4,613,415 A (WREATH et al) 23 SEPTEMBER 1986, See Abstract.

US 4,324,635 A (SWEENEY) 13 APRIL 1982, See Abstract.

US 4,554,367 A (WEHNER et al) 19 NOVEMBER 1985, see col. 5, lines 10-17 and col. 6, lines 20-21.

US 3,819,329 A (KAESTNER et al) 25 JUNE 1974, see col. 8-9 and Figure 3.

22. The generator of Claim 2, further comprising a gas sparger, located in the demister trap prior to the line connecting the demister trap to the drainage tank.
23. The generator of Claim 2, further comprising a pressure relief means located on the demister trap.
24. The generator of Claim 23, wherein the pressure relief means a rupture disk.
25. A disinfecting mist consisting essentially of gaseous chlorine dioxide, an inert gas selected from the group consisting of air, carbon dioxide, helium and nitrogen, wherein the amount of gaseous chlorine dioxide is about 0.0001 to less than 10% by volume, wherein the amount of the inert gas is about 90% to about 99.9% by volume, and wherein the water vapor is about 1 to about 20% by volume.
26. The mist of Claim 25, wherein the inert gas is air.
27. A method of disinfecting crops using the mist of Claim 25.
28. The method of Claim 27, wherein the crops are fresh produce, grains, or tobacco.
29. The method of Claim 28, wherein the produce includes vegetables and fruits.
30. A method of disinfecting clay using the mist of Claim 25.
31. A method of disinfecting fields, greenhouses, storage cellars, agricultural equipment, and ventilation equipment using the mist of Claim 25.
32. A method of disinfecting porous surface using the mist of Claim 25.
33. The method of Claim 32, wherein the porous surface is wood or concrete.
34. An electrolytic process for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor, which process comprises the steps of:
  - (a) feeding a buffered aqueous alkali metal chlorite solution into the anolyte compartment of an electrolytic generator;
  - (b) feeding water into the catholyte compartment of the electrolytic generator;
  - (c) supplying a motive inert gas to an eductor to create a vacuum in the anolyte compartment; and
  - (d) recovering the mist from the anolyte compartment.
35. The method of Claim 34, further comprising the steps of supplying a motive inert gas to an eductor to create a vacuum in the catholyte compartment.

**AMENDED SHEET**

## PCT

REC'D 27 NOV 2001

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 3041-022	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/23911	International filing date (day/month/year) 01 SEPTEMBER 2000	Priority date (day/month/year) 03 SEPTEMBER 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant INTERNATIONAL IOXIDE, INC		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets.
- ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 0 sheets.

## 3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03 APRIL 2001	Date of completion of this report 08 NOVEMBER 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-8230	Authorized officer DONALD R. VALENTINE Telephone No. (703) 308-0661 DEBORAH THOMAS PARALEGAL SPECIALIST

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

## I. Basis of the report

### 1. With regard to the elements of the international application: \*

☒ the international application as originally filed

☒ the description:

pages 1-22, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the claims:

pages 23-27, as originally filed  
pages NONE, as amended (together with any statement) under Article 19  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the drawings:

pages 1-9, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

☒ the sequence listing part of the description:

pages NONE, as originally filed  
pages NONE, filed with the demand  
pages NONE, filed with the letter of

### 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item. These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

### 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

### 4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages NONE  
☒ the claims, Nos. NONE  
☒ the drawings, sheets/fig. NONE

### 5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. statement**

Novelty (N)	Claims	<u>1-24, 26-27, 35-36</u>	YES
	Claims	<u>25, 28-30</u>	NO
Inventive Step (IS)	Claims	<u>1-24, 26-27, 35-36</u>	YES
	Claims	<u>25, 28-34</u>	NO
Industrial Applicability (IA)	Claims	<u>1-36</u>	YES
	Claims	<u>NONE</u>	NO

**2. citations and explanations (Rule 70.7)**

Claim 25 lacks novelty under PCT Article 33(2) as being anticipated by Cawfield et al.  
See col. 5, lines 10-25.

Claim 25 lacks an inventive step under PCT Article 33(3) as being obvious over Cawfield et al.  
The reagent mixed with water vapor is considered to be an obvious form of a "mist".

Claims 25 and 28-30 lack novelty under PCT Article 33(2) as being anticipated by Wehner et al.  
See col. 4, lines 15-47; col. 5, lines 10-16 and lines 40-55; col.6, line 20.

Claims 25, 28-34 lack an inventive step under PCT Article 33(3) as being obvious over Wehner et al.  
The reference defines the product chlorine dioxide as suitable for administering to plant life as well as other inanimate objects. It would be considered within the skill of the art to apply this substance to other materials needing to be appropriately treated because the chlorine dioxide has been demonstrated at being useful for this purpose. No unexpected results would be apparent.

Claims 1-24 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest an electrolytic generator for generating chlorine dioxide which comprises, in combination, a high surface area porous anode; corrosion resistant cathode; cation ion exchange membrane separating anode and cathode into anode and cathode compartments; an array of non-corrosive support ribbing for the membrane; catholyte and anolyte cell frames with inlets and outlets; anolyte infeed means; inlet means for softened, deionized or demineralized purge water including a line with a solenoid (Continued on Supplemental Sheet.)

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/23911

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

### CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): A01N 2/08, 25/06; C25B 1/24, 9/00, 11/00, 11/04, 11/12, 15/00 and US Cl.: 204/230.3, 230.5, 265, 266, 284, 290.12, 290.14, 291, 292, 293, 294; 205/556, 701; 422/28; 424/40

### V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

followed by a rotameter and a flow switch; catholyte infeed means; ascending anolyte outfeed means; an eductor connected to the anolyte infeed means; motive water infeed means; catholyte outfeed means; sensor connected to the anolyte outfeed means prior to the eductor; pressure switch on the motive infeed means; and D.C. power supply and automatic current interrupter for preventing reverse current flow across the cell upon shutdown. Further, the prior art does not show or suggest a method for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor which comprises feeding buffered aqueous alkali metal solution to the anolyte compartment of an electrolytic generator, feeding water to the generator catholyte compartment, supplying motive inert gas to an eductor to create a vacuum in the anolyte compartment and recovering the mist from the anolyte compartment.

Claims 1-36 meet the criteria set out in PCT Article 33(4), because the invention has industrial applicability in the area of disinfecting food stuffs, fields, greenhouses, storage cellars, and autoclaves.

### ----- NEW CITATIONS -----

US 4,613,415 A (WREATH et al) 23 SEPTEMBER 1986, See Abstract.

US 4,324,635 A (SWEENEY) 13 APRIL 1982, See Abstract.

US 4,554,367 A (WEHNER et al) 19 NOVEMBER 1985, see col. 5, lines 10-17 and col. 6, lines 20-21.

US 3,819,329 A (KAESTNER et al) 25 JUNE 1974, see col. 8-9 and Figure 3.

PATENT COOPERATION TREATY  
**FILE COPY 409**

**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

Form PCT/IPEA/409 (cover sheet) (July 1998) FILE COPY - DO NOT MAIL

Applicant's or agent's file reference 5041-022	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/23911	International filing date (day/month/year) 01 SEPTEMBER 2000	Priority date (day/month/year) 03 SEPTEMBER 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant INTERNATIONAL IOXIDE, INC		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of \_\_\_\_\_ sheets.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of \_\_\_\_\_ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03 APRIL 2001	Date of completion of this report 01 FEBRUARY 2002
Facsimile No. (703) 305-3230	Authorized officer AND Telephone No.  DONALD R. VALENTINE (703) 308-0681



INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
Form PCT/IPEA/409 (Rev. 1) (July 1998)  
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International application No.

PCT/US00/23911

I. Basis of the report

1. With regard to the elements of the international application:\*

☐ the international application as originally filed

☒ the description:

pages 1-22, as originally filed

pages NONE, filed with the demand

pages NONE, filed with the letter of

☒ the claims:

pages 23-26, as originally filed

pages NONE, as amended (together with any statement) under Article 19

pages 27, filed with the demand

pages NONE, filed with the letter of

☒ the drawing:

pages 1-9, as originally filed

pages NONE, filed with the demand

pages NONE, filed with the letter of

☒ the sequence listing part of the description:

pages NONE, as originally filed

pages NONE, filed with the demand

pages NONE, filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.  
These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form:

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. NONE

☒ the drawings, sheets/fig. NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box II) (July 1998)

FILE COPY - DO NOT MAIL

International application No.

PCT/US00/23911

II. Priority

1. ☐ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:
- ☐ copy of the earlier application whose priority has been claimed.
  - ☐ translation of the earlier application whose priority has been claimed
2. ☐ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box III) (July 1998)  
FILE COPY - DO NOT MAILInternational application No.  
PCT/US00/23911

## III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been and will not be examined in respect of:

☐ the entire international application.☐ claims Nos. \_

because:

☐ the said international application, or the said claim Nos. \_ relate to the following subject matter which does not require international preliminary examination (*specify*).☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. \_ are so unclear that no meaningful opinion could be formed (*specify*).☐ the claims, or said claims Nos. \_ are so inadequately supported by the description that no meaningful opinion could be formed.☐ no international search report has been established for said claims Nos. \_.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.☐ the computer readable form has not been furnished or does not comply with the standard.

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box IV) (July 1998)  
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International application No.

PCT/US00/23911

## IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☐ paid additional fees.
- ☐ paid additional fees under protest.
- ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- ☐ complied with.
- ☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report

- ☐ all parts.
- ☐ the parts relating to claims Nos. .

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/408 (Box V) (July 1998)  
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International application No.

PCT/US00/23911

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. statement

## Novelty (N)

Claims	<u>1-35</u>	YES
Claims	<u>NONE</u>	NO

## Inventive Step (IS)

Claims	<u>1-35</u>	YES
Claims	<u>NONE</u>	NO

## Industrial Applicability (IA)

Claims	<u>1-35</u>	YES
Claims	<u>NONE</u>	NO

## 2. citations and explanations (Rule 70.7)

Claims 1-35 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest an electrolytic generator for generating chlorine dioxide which comprises, in combination, a high surface area porous anode; corrosion resistant cathode; cation ion exchange membrane separating anode and cathode into anode and cathode compartments; an array of non-corrosive support ribbing for the membrane; catholyte and anolyte cell frames with inlets and outlets; anolyte infeed means; inlet means for softened, deionized or demineralized purge water including a line with a solenoid followed by a rotameter and a flow switch; catholyte infeed means; ascending anolyte outfeed means; an eductor connected to the anolyte infeed means; motive water infeed means; catholyte outfeed means; sensor connected to the anolyte outfeed means prior to the eductor; pressure switch on the motive infeed means; and D.C. power supply and automatic current interrupter for preventing reverse current flow across the cell upon shutdown. Further, the prior art does not show or suggest a method for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor which comprises feeding buffered aqueous alkali metal solution to the anolyte compartment of an electrolytic generator, feeding water to the generator catholyte compartment, supplying motive inert gas to an eductor to create a vacuum in the anolyte compartment and recovering the mist from the anolyte compartment.

Claims 1-35 meet the criteria set out in PCT Article 33(4), because the invention has industrial applicability in the area of disinfecting food stuffs, fields, greenhouses, storage cellars, and autoclaves.

NEW CITATIONS

(Continued on Supplemental Sheet.)

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box VI) (July 1998)  
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International application No.

PCT/US00/23911

## VI. Certain documents cited

## 1. Certain published documents (Rule 70.10)

Application No.  
Patent No.Publication Date  
(day/month/year)Filing Date  
(day/month/year)Priority date (valid claim)  
(day/month/year)

## 2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosureDate of non-written disclosure  
(day/month/year)Date of written disclosure  
referring to non-written disclosure  
(day/month/year)

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box VII) (July 1998)  
FILE COPY - DO NOT MAIL

International application No.

PCT/US00/23911

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/409 (Box VIII) (July 1996)

FILE COPY - DO NOT MAIL

International application No.

PCT/US00/23911

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Form PCT/IPEA/ (Supplemental Box) (July 1996)  
FILE COPY NOT MAIL

International application No.

P 500/23911

## Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

## CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): A01N 2/08, 25/06; C25B 1/24, 9/00, 11/00, 11/04, 11/12, 15/00 and US Cl.: 204/230.3, 230.5, 265, 266, 284, 290.12, 290.14, 291, 292, 293, 294; 205/556, 701; 422/28; 424/40

## V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

US 4,613,415 A (WREATH et al) 23 SEPTEMBER 1986, See Abstract.

US 4,324,635 A (SWEENEY) 13 APRIL 1982, See Abstract.

US 4,554,367 A (WEHNER et al) 19 NOVEMBER 1985, see col. 5, lines 10-17 and col. 6, lines 20-21.

US 3,819,329 A (KAESTNER et al) 25 JUNE 1974, see col. 8-9 and Figure 3.

## PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: MARGARET B. KELLEY  
CLIFFORD CHANCE ROGERS & WELLS LLP  
200 PARK AVENUE  
NEW YORK, NY 10166

## FILE COPY 416

NOTIFICATION OF TRANSMITTAL OF  
INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Form PCT/IPEA/416(July 1992) DO NOT MAIL

Date of Mailing  
(day/month/year)

Applicant's or agent's file reference

3041-022

## IMPORTANT NOTIFICATION

International application No.

PCT/US00/23911

International filing date (day/month/year)

01 SEPTEMBER 2000

Priority Date (day/month/year)

03 SEPTEMBER 1999

Applicant

INTERNATIONAL IOXIDE, INC

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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DONALD R. VALENTINE

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(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number  
**WO 01/18279 A1**

- (51) International Patent Classification<sup>7</sup>: C25B 1/26, A61L 9/14
- (21) International Application Number: PCT/US00/23911
- (22) International Filing Date:  
1 September 2000 (01.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/389,335 3 September 1999 (03.09.1999) US
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:  
US Not furnished (CIP)  
Filed on Not furnished
- (71) Applicant (for all designated States except US): INTERNATIONAL DIOXIDE, INC. [US/US]; 554 Ten Rod Road, North Kingston, RI 02852 (US).
- (72) Inventors; and  
(75) Inventors/Applicants (for US only): KRAFTON, Brian, D. [US/US]; 25 Paddock Court, Wakefield, RI 02879 (US). SMEDLEY, John, C. [US/US]; 5707 N.W. Oakridge Court, Platte Woods, MO 64151 (US). KUCHER, Donald, C. [US/US]; 1520 Oak Lane, Quackertown, PA 18951 (US).
- (74) Agent: KELLEY, Margaret, B.; Clifford Chance Rogers & Wells LLP, 200 Park Avenue, New York, NY 10166 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A GENERATOR FOR GENERATING CHLORINE DIOXIDE UNDER VACUUM EDUCTION IN A SINGLE PASS

(57) Abstract: A vacuum operated electrolytic generator can be used to produce a chlorine dioxide solution or a mist of chlorine dioxide from a buffered aqueous alkali metal chlorite solution in one pass through an electrolytic cell. The cell contains a high surface area anode, a corrosion-resistant highly conductive cathode, and a cation ion exchange membrane between the anode and cathode. An eductor is used on the anolyte effluent line to create a vacuum and draw the anolyte through the cell. Either motive water or a motive inert gas (such as air) is used in the eductor. Preferably, an eductor is used in the catholyte effluent line. An ascending anolyte effluent line with a non-corrosive check valve leads from the cell to the anode eductor. Sensors are used to monitor the composition of the anolyte effluent and/or the anolyte feed. The final product is a chlorine dioxide solution when water is used for the eduction. The final product is a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor when an inert gas is used for the eduction. The mist is useful for application crop, soils, produce such as vegetables, fruit, and tobacco, fields, storage cellars, and the like.

WO 01/18279 A1

A Generator For Generating Chlorine  
Dioxide Under Vacuum Eduction In A Single Pass

Cross-Reference to Related Application

This application is a continuation-in-part application of Serial No. 09/289,335 filed September 3, 1999.

Background of the Invention

This invention relates generally to the production of chlorine dioxide. More particularly, it relates to an electrolytic generator used to manufacture chlorine-free chlorine dioxide from alkali metal chlorite solutions.

Chlorine dioxide is commercially employed as a bleaching, fumigating, sanitizing or sterilizing agent. Chlorine dioxide can be used to replace the chlorine and hypochlorite products more traditionally used in such applications with resultant benefits. Chlorine dioxide is a more powerful sterilizing agent and requires lower dose levels than chlorine at both low pHs and high pHs, although it is not particularly stable at high pH levels. More importantly, chlorine dioxide produces lower levels of chlorinated organic compounds than chlorine when it is used to sterilize raw water containing organic compounds. Additionally, chlorine dioxide is less corrosive than chlorine to metals.

The electrolytic production of chlorine dioxide is old and well known. See U.S. Pat. No. 2,163,793 issued Jun. 27, 1939 (J. O. Logan); British Patent No. 714,828 published Sept. 1, 1954 (Farbenfabriken Bayer); U.S. Patent No. 2,717,237 issued Sept. 6, 1955 (Rempel); Japanese Patent Application No. 81-158883, published Dec. 7, 1981; and U.S. Patent No. 4,542,008 issued Sep. 17, 1985 (Capuano et al.).

U.S. 5,084,149 (issued January 28, 1992 to J.J. Kaczur et al. discloses an electrochemical process for manufacturing chlorine-free chlorine dioxide from a diluted alkali metal chlorite solution containing a conductive salt additive in a single step. The electrolytic cell used contains a porous flow-through anode and a cathode separated by a suitable separator.

U.S. 5,092,970 and U.S. 5,106,465 (issued April 21, 1992 to J.J. Kaczur et al.) discloses a process for electrolytically producing an aqueous solution of chlorine dioxide in a electrolytic cell having an anode compartment, a cathode compartment, and at least one cation ion exchange

compartment between the anode and cathode compartments. An aqueous solution of an alkali metal chlorite is fed to the ion exchange compartment. The anolyte in the anode compartment is electrolyzed to generate hydrogen ions. The hydrogen ions are passed from the anode compartment through the membrane into the ion exchange compartment to displace alkali metal ions and produce an aqueous solution of chlorine dioxide. The alkali metal ions from the ion exchange compartment are passed into the cathode compartment.

In the '465 patent, the use of additives or activators in the chlorite feed solution is disclosed. The additives or activators promote more efficient conversion of chlorite to chlorine dioxide and suppress chlorate formation. Suitable additives include inorganic alkali metal salts and/or chlorides, phosphates, and sulfates and alkali metal tartrates and citrates.

U.S. 5,294,319 (issued March 15, 1994 to J.J. Kaczur et al.) discloses a porous high surface area electrode particularly suitable for use in electrochemical processes.

A disadvantage of the above electrolytic processes is the production of the chlorine dioxide in the anode compartment of the generator so that the chlorine dioxide must be recovered from the anolyte by stripping with air or by some other appropriate means.

The generation and use of chlorine dioxide solutions poses a significant problem because the generation of chlorine-free chlorine dioxide is complex and requires a number of purification steps, including the stripping step discussed above and reabsorption of chlorine dioxide from a generating solution to a receiving solution. A stream of air is frequently used for this purpose; however, operation of such a process is hazardous if the chlorine dioxide concentrations in the air become high enough to initiate spontaneous decomposition. U.S. Patent No. 4,683,039 (Twardowski et al.) discloses a purification method involving the use of a gas-permeable hydrophobic membrane. This purification method reduces the risk of chlorine dioxide decomposition but requires additional costly equipment.

The above problems were solved by employing a continuous electrochemical process and an electrolytic cell containing a porous flow-through anode. Chlorine-free chlorine dioxide was produced in a concentration of at least about 2 to about 10 grams per liter from dilute alkali metal chlorite solutions in a single step. This process and the cell are described in U.S. 5,158,658 issued October 27, 1992 (Cawfield et al.), the disclosure of which is incorporated herein by reference.

#### Summary of the Invention

The present invention provides an electrolytic generator, operated under a vacuum, for producing a solution of chlorine dioxide or a mist containing gaseous chlorine dioxide in one pass by the electrolysis of an anolyte which is a buffered aqueous alkali metal chlorite solution. The

vacuum is provided by an eductor. When a chlorine dioxide solution is generated, the motive force in the eductor is water. When a chlorine dioxide-containing mist is generated, the motive force in the eductor is a cool, dry inert gas such as carbon dioxide, helium, nitrogen, oxygen, or preferably air.

When the generator is used to produce the chlorine dioxide solution, the generator comprises in combination:

(a) a high surface area, porous anode with multiple electrode posts; (b) a corrosion-resistant, highly conductive cathode with multiple electrode posts; (c) a cation ion exchange membrane which separates the anode and the cathode and forms an anolyte compartment and a catholyte compartment; (d) an array of non-corrosive support ribbings for the cation exchange membrane; (e) a non-blinding mesh spacer between the cation exchange membrane and the cathode; (f) catholyte and anolyte cell frames with inlet ports to the catholyte and anolyte compartments at the bottom of the cell frames, with outlet ports from the catholyte and anolyte compartments at the top of the cell frames, and with internal flow distribution headers enclosing the anolyte and catholyte compartments; (g) an anolyte infeed means for introducing the buffered aqueous alkali metal chlorite anolyte into the anolyte compartment, which infeed includes a line with a solenoid followed by a rotameter and a flow switch; (h) an inlet means for softened, deionized, or demineralized purge water, which means includes a line with a solenoid followed by a rotameter and a flow switch, which means is connected to the anolyte infeed line by a juncture and a line leading from the juncture to the anolyte inlet port; (i) a catholyte infeed means for introducing softened, deionized, or demineralized water to the catholyte port, which means includes a line with a solenoid followed by a rotameter and a flow switch; (j) an ascending anolyte outfeed means, connected to the cell frame at the top on the anolyte side, to remove the aqueous chlorine dioxide anolyte effluent from the anolyte outlet port; (k) an eductor connected to the anolyte outfeed means for creating a vacuum in the anolyte compartment by which the anolyte is drawn through the anolyte compartment; (l) a motive water infeed means for supplying water to the eductor; (m) a catholyte outfeed means, connected to the catholyte outlet port, to remove the alkaline hydroxide catholyte effluent containing entrained hydrogen, which means has a non-corrosive check valve (e.g., a plastic check valve) before the eductor; (n) a sensor, connected to the anolyte outfeed means prior to the eductor, for monitoring the anolyte effluent; (o) a pressure switch on the motive water infeed means; and (p) a DC power supply and an automatic current interrupter to prevent reverse current flow across the cell upon shutdown.

When the electrolytic generator, is used to produce a mist containing gaseous chlorine dioxide, the generator comprises in combination:

(a) a high surface area, porous anode with multiple electrode posts; (b) a corrosion-resistant, highly conductive cathode with multiple electrode posts; (c) a cation ion exchange membrane which separates the anode and the cathode and forms an anolyte compartment and a catholyte compartment; (d) an array of non-corrosive support ribbings for the cation exchange membrane; (e) a non-blinding mesh spacer between the cation exchange membrane and the cathode; (f) catholyte and anolyte cell frames with inlet ports to the catholyte and anolyte compartments at the bottom of the cell frames, with outlet ports from the catholyte and anolyte compartments at the top of the cell frames, and with internal flow distribution headers enclosing the anolyte and catholyte compartments; (g) an anolyte infeed means for introducing the buffered aqueous alkali metal chlorite anolyte into the anolyte compartment, which infeed includes a line with a solenoid followed by a rotameter and a flow switch; (h) an inlet means for softened, deionized, or demineralized purge water, which means includes a line with a solenoid followed by a rotameter and a flow switch, which means is connected to the anolyte infeed line by a juncture and a line leading from the juncture to the anolyte inlet port; (i) a catholyte infeed means for introducing softened, deionized, or demineralized water to the catholyte port, which means includes a line with a solenoid followed by a rotameter and a flow switch; (j) an ascending anolyte outfeed means, connected to the cell frame at the top on the anolyte side, to remove the aqueous chlorine dioxide anolyte effluent from the anolyte outlet port; (k) an eductor connected to the anolyte outfeed means for creating a vacuum in the anolyte compartment by which the anolyte is drawn through the anolyte compartment; (l) a motive gas infeed means for supplying an inert gas to the eductor; (m) a catholyte outfeed means, connected to the catholyte outlet port, to remove the alkaline hydroxide catholyte effluent containing entrained hydrogen, which means has a non-corrosive check valve before the eductor; (n) a sensor, connected to the anolyte outfeed means prior to the eductor, for monitoring the anolyte effluent; (o) a pressure analyzing means on the gas infeed means of the generator; (p) a DC power supply and an automatic current interrupter to prevent reverse current flow across the cell upon shutdown; (q) a pressure relief means on the anolyte outfeed means; (r) a temperature analyzing means on the anolyte outfeed means; (s) a pressure analyzing means on the anolyte outfeed means; (t) a gas flow analyzing means on the anolyte outfeed means; (u) an analyzing means for determining the chlorine dioxide gas present in the anolyte; and (v) a back pressure valve on the anolyte outfeed means.

Suitable anodes for the generators include a fine fibrous conductive substrate, such as titanium, niobium, zirconium, tantalum, aluminum, tungsten, or hafnium, which is optionally coated

with an electrocatalyst selected from precious metals (e.g., platinum, silver, or gold), the oxides of platinum group metals, (e.g., the oxides of ruthenium, rhodium, palladium, iridium, or osmium), mixtures thereof, or alloys thereof. The anode can be a segmented or unsegmented fibrous titanium anode coated with platinum. The cathode can be a perforated stainless steel plate.

A dilution water infeed means for introducing softened, deionized, or demineralized water into the anolyte infeed line and a juncture joining the dilution water infeed means and the anolyte infeed means are optional. The anolyte in the generator, prior to dilution is about 0.01 to about 31% by weight of sodium chlorite buffered at about pH 9.0.

Also optional are eductors connected to the catholyte outfeed line for creating a vacuum in the catholyte compartment, connected to the dilution water infeed means for creating a vacuum to draw the water into dilution water infeed means; a sensor connected to the anolyte infeed means for monitoring the anolyte infeed; and an on/off valve for the motive water. The catholyte and anolyte infeed and outfeed lines can be plastic tubings (e.g., polyethylene tubings).

Further optional components for use with the generators are an electrical panel containing a sensor, safety indicators, and operation controls. The sensor can be a pH meter, a conductivity probe, an oxidation-reduction potential probe, an amperometric detector, and a colorimetric absorption indicator. Further optional components for use when the inert gas is used as the motive force include a demister trap on the anolyte outfeed means after the back pressure valve which is used to remove excess water vapor from the diluted anolyte effluent stream. The demister trap comprises a demister body, a pressure relief device, a demister packing, an effluent inlet port for the diluted anolyte, exit port for the demisted diluted anolyte, an inlet means for a sparging gas, a gas sparging device, collection sump for the condensed water vapor, a sump level indication device, a water purge port, an automatic sump purge valve, and a discharge line connecting the demister trap to a drainage tank for neutralizing the condensed water vapor.

The present electrolytic generators are distinguished from prior electrolytic cells by the use of a single anolyte eductor or more preferably two separate eductors to generate the vacuum required to draw the anolyte and catholyte feeds through the electrolytic cell. The use of the eductors to create a vacuum in the electrolytic cell allows one to use more concentrated alkali metal chlorite solutions as the anolyte feed. For example, in the vacuum electrolytic generator the anolyte feed can be about 2% or greater by weight of sodium chlorite. In non-vacuum electrolytic cells the anolyte feed can only be 1% by weight of the sodium chlorite. One or more sensors monitor the constituents in the anolyte effluent and/or anolyte feed.

When an inert gas is used as the motive force, the eductor motive pressure is about 1 to 100 psig and the back pressure is about 20-80% of its motive pressure. The motive gas flow can be



varied as required by the end use application. The temperature of the motive gas is from 0° to about 60°C.

The present electrolytic generators also incorporates a number of safety features such as a purge of the generator after the system shuts down or is turned off with softened deionized, or demineralized water, an anolyte effluent line which progressively ascends, without looping back, to the inlet of the anolyte eductor, and sensors to monitor the reaction. The water purge quickly and effectively evacuates the concentrated chlorine dioxide from the anode compartment of the electrolytic generator after the generator shut down. The ascending anolyte effluent line minimizes the possibility that gaseous pockets of chlorine dioxide will form. Such gaseous pockets of chlorine dioxide are potentially explosive. The pH, the electrical conductivity, the oxidation-reduction potential (ORP), the current (amps), or color of the anolyte effluent can be measured using a suitable sensor. The electrical conductivity, current, or OPR of the anolyte infeed can also be measured. If desired, both the infeed and effluent can be monitored.

Another advantage of the vacuum operated electrolytic generators is that it is not necessary to separately remove hydrogen gas produced in the reaction from the catholyte effluent. The entrained hydrogen gas does not impede the cathode effluent flow and does not need to be separated as was customary in prior art electrolytic processes.

The present invention also provides a disinfecting mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor, where the amount of gaseous chlorine dioxide is about 0.0001 to less than 10% by volume, i.e., 1 to less than 100,000 ppm, where the amount of the inert gas is about 90% to about 99.9% by volume, and where the water vapor is about 1% to about 20% by volume. The inert gas is selected from the group consisting of air, carbon dioxide, helium, nitrogen, and oxygen. Air is preferred. As used herein, the word "mist" is intended to include a vapor, a gas, or a mist which will depend on the temperature of the inert gas which can range from 0°C to about 60°C.

The present invention also provides a method of disinfecting crops such fresh produce, e.g., vegetables and fruits, grains, or tobacco using the mist containing the gaseous chlorine dioxide. When used on crop soils, the mist kills both the unwanted plants (i.e., weeds) as well as their seeds. The mist can also be used to disinfect clay or to disinfect fields, greenhouses, storage cellars, agricultural equipment, and ventilation equipment. The mist can also be used to disinfect non-porous surfaces, but it is particularly effective on porous surfaces such as wood, concrete, and the like.

The present invention further provides an electrolytic process for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor, which process comprises the steps of:

- (a) feeding a buffered aqueous alkali metal chlorite solution into the anolyte compartment of an electrolytic generator;
- (b) feeding water into the catholyte compartment of the electrolytic generator;
- (c) supplying a motive inert gas to an eductor to create a vacuum in the anolyte compartment; and
- (d) and recovering the mist from the anolyte compartment. Preferably, a motive inert gas is supplied to an eductor to create a vacuum in the catholyte compartment.

#### Description of The Drawings

Figure 1 schematically depicts an electrolytic generator, such as that used in the Cawfield et al. process, for producing an aqueous solution of chlorine dioxide in a single pass using an anolyte feed which can be diluted during operation of the generator. The generator is operated under a vacuum created by a single anolyte eductor or more preferably by separate anolyte and catholyte eductors jointly connected to a motive water line. The preferred eductors and motive water inlet are shown on the left side of figure 1. The electrolytic cell is shown in the center of figure 1. The cell contains a high surface area anode and a perforated cathode separated by a cation permeable ion exchange membrane. The membrane divides the cell into catholyte and anolyte compartments having inlets at the bottom for the anolyte and catholyte feed and outlets at the top for the anolyte and catholyte effluents. The membrane is supported on the anode side of the cell by an array of non-corrosive support ribs. These ribs minimize deflection of the membrane towards the anode chamber of the cell where compression of segmented or unsegmented high surface area anode could occur. A non-blinding mesh spacer separates the membrane from the cathode. The feed lines and flow switches for the anolyte feed, catholyte feed, dilution water and water purge are shown on the lower right of figure 1. The anolyte feed consists of an undiluted, buffered aqueous alkali metal chlorite solution, e.g., an aqueous solution of 5 wt. % sodium chlorite buffered to about pH 9.0 with buffers, e.g., sodium carbonate/sodium bicarbonate, sodium diphosphates/sodium hydrogen phosphate, citrates, and the like. The catholyte feed consists of softened deionized, or demineralized water. Softened, deionized or demineralized water is also used for the anolyte feed dilution and purge feed.

The control panel shown on the upper right hand side of the figure contains the operating controls and programmable controller for monitoring safety switches, and sensor(s) used for monitoring the constituents in the anolyte effluent and/or in the anolyte feed.

Figure 1A schematically depicts an electrolytic generator for producing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor. In addition to the elements shown in Figure 1, it includes a means (103) for releasing pressure, preferably a rupture disk; a means (104) for measuring the temperature of the chlorine dioxide-containing mist, such as a thermocouple with an isolation well; a means (105) for measuring the pressure, such as a pressure transducer with an isolation well; a means (106) for the measuring gas flow, such as a gas meter; a means (107) for analyzing the amount of chlorine dioxide gas in the mist, such as a scattered light photometer; and a back pressure valve (108) for regulating the back pressure imposed on the anolyte eductor (10). These means, i.e., 103 to 107 must be located upstream of the back pressure valve (108). They may be located in the pipe leading from the anolyte eductor outlet (10) to the demister trap (109).

The demister tank has an inlet (110) near the top for introducing the chlorine dioxide mist, an outlet (111) for the demisted chlorine dioxide gas, a waste water drain (112) in the bottom, a gas sparger inlet (113) and gas sparger element (114) near the bottom of the collection sump (115), a level control means (116) such as a level switch and solenoid (117) for controlling the level of condensed water in the collection sump, a drain line (118) for transfer of the waste stream to the neutralization tank, a demister packing (119), and a pressure relief means (120) such as a rupture disk.

Figure 2 shows the input line (1) is for the motive water feed. On/off valve (2) controls for the motive water feed. Pressure gauge (3) and pressure switch (4) monitoring the motive water pressure and provide an alarm signal for undesirable pressure conditions. Conduit line (5) runs from pressure switch (4) to the electrical panel. The pressure releasing means (103), the temperature measuring means (104), the pressure measuring means (105), the gas flow measuring means (106), and the chlorine dioxide gas measuring means (107) shown in Figure 6. Solenoid (6) is connected to motive water line (1). Conduit line (7) runs from solenoid (6) to the electrical panel shown in Figure 6. Union (8) joins the catholyte eductor (9) and anolyte eductor (10). Eductor (9) and (10) create sufficient vacuum to draw the catholyte and anolyte flows through the electrochemical cell. Inline ball check valves (11) and (12), respectively, prevent back flow through eductors (9) and (10). Catholyte and anolyte effluents are educted from the electrolytic cell through plastic tubings (13) and (14), respectively. The anolyte effluent tubing (14) progressively ascends, with no back looping or horizontal sections, to the inlet of anolyte eductor (10) so as to minimize the possible formation of gaseous pockets of chlorine dioxide. Such pockets are potentially explosive. Non-corrosive check valves (15) and (16), respectively, are present on the catholyte and anolyte tubings (13) and (14), respectively, to prevent back flow through the

electrolytic cell and prevent inadvertent over hydraulic pressurization of the cell. Optional sample taps are typically located on the catholyte and anolyte discharge lines as illustrated.

Figure 3 shows electrolytic cell (17) and cell enclosure (18). The sensor shown is pH probe (30) which is used to monitor anolyte effluent. Although not shown, other sensors can be used to monitor anolyte effluent. In addition, (also not shown) an ORP detected conductivity sensor could be used to monitor the anolyte feed. Inlet (19) for the anolyte feed, which is the diluted buffered aqueous alkali metal chlorite solution, leads into the anolyte compartment (20). Inlet (21) for the catholyte feed, which is the softened or demineralized water, leads into the catholyte compartment (22). Water purge feed line (23) is connected to the diluted anolyte feed line (19). Exit (24) for the catholyte effluent is connected by tubing (13) to the catholyte eductor (9) through check valve (15). Catholyte effluent vacuum gauge (25) is located after exit (24). Exit (26) for the anolyte effluent is connected by tubing (28) to probe holder (29) where a probe (30) is inserted to measure the pH, electrical conductivity, or oxidation-reduction potential of the anolyte effluent before it enters tubing (14) for eduction into the anolyte eductor (10) through check valve (16). Anolyte effluent vacuum gauge (27) is located between exit (26) and the sensor holder (29) and sensor (30). Sensor (30) is connected to the control panel shown in Figure 7.

Figure 4 shows the configuration of the interior of the electrolytic cell (17). The anolyte inlet port (31) and anolyte outlet port (32) are shown on the right. The catholyte inlet port (33) and exit port (34) are shown on the left. Between the anode cell frame (35) and the high surface area anode (36) is an anode backing plate (37) and a perimeter-sealing plastic gasket (38). Catholyte inlet and outlet ports (33 and 34) are shown on the left side of cell frame (39). Between the cell frame (39) and the perforated cathode (40) is a cathode backing mesh (41) and a plastic gasket (42). Between the high surface area anode (36) and the mesh spacer (43) is cation exchange membrane (44). Also shown are the membrane support ribbings (45), cathode conductor post fittings (46), anode conductor post fittings (47), cathode and anode current splitters (48) and (49), and cathode and anode conductor post nuts. The cathode conductor post fittings (46) provide a liquid tight seal around the cathode conductor posts (50). The anode conductor post fittings (47) provide a liquid tight seal around the anode conductor posts (51).

Figure 5 shows the high surface area anode (36) segmented into sections to fit into each of the corresponding areas of the membrane support ribbing (45). The membrane ribbing support (45) is designed to provide adequate support of the cation exchange membrane (44) while allowing free flow of anolyte through the anode cell frame (35) from the anode inlet port (31) to the anode outlet port (32).

Figure 6 shows the distribution header arrangement (52) with multiple flow ports for the cathode inlet port (33). Similar distribution header arrangements are present for the anode inlet port (31), cathode inlet port (34), and anode outlet port (32). The design of the distribution header is such that there is a sufficient pressure drop across the header to ensure evenly distributed flow through each distribution header and each individual flow port.

Figure 7 shows the feed lines to the electrolytic cell (17). Catholyte water feed line (53) is controlled by on/off valve (54). The catholyte water then passes through solenoid (55) to flow controlling rotameter (56) through flow switch (57) and into tubing (58) which leads into catholyte inlet check valve (21) of the electrolytic cell frame (22). Anolyte feed line (59) passes undiluted anolyte chlorite feed through on/off valve (60). The undiluted anolyte feed passes through solenoid (61) to flow controlling rotameter (62) and through flow switch (63) and into tubing (64) which leads to junction (65). Anolyte water feed line (66), which provides the softened, deionized, or demineralized water for diluting the buffered alkali metal chlorite introduced into the anolyte feedline (59) passes through on/off valve (67). The softened, deionized or demineralized water passes through solenoid (68) to rotameter (69), through flow switch (70), and into tubing (71) which connects with junction (64). From junction (64) the diluted anolyte passes through tubing (72) into the anolyte inlet of the anode electrolytic cell frame (20). Non-corrosive (e.g., Teflon) check valve (13) eliminates possible back flow of anolyte through inlet of the anode electrolytic cell frame (20). A water purge for the anolyte chamber (20) is introduced through inlet (73), pressure regulator (74), pressure gauge (75) into solenoid (76), flow control valve (77), and flow switch (78). A non-corrosive (e.g., plastic) feed line (79), leads through a non-corrosive check valve (e.g., Teflon) (80) into junction (81) joining the diluted anolyte feed line before it enters inlet tubing (15) of the electrolytic cell frame (20).

Figure 8 shows the control panel (82) which contains probe controller (83), shown here as a pH meter, in the center. Operator touch pads (84), (85), (86), (87), and (88) are for start/stop, automatic operation booster pump on, alarm silencer, and alarm reset, respectively. Indicators (89), (90), and (91) are for alarm, purge, and run, respectively. Sensor connection (92) leads into control panel (82). Solenoid conduits (93), (94), (95), (96), and (97) are for the motive eductor water, catholyte water, undiluted anolyte feed, anolyte dilution water, and purge water, respectively. Pressure switch conduit (98) relays the electrical signal to the control panel (82) to monitor the motive water pressure. Flow switch conduits (99), (100), (101), and (102) are for relaying the respective electrical signals between flow switches (57), (70), (63), (78) and the control panel (82).

Other features and advantages of the present invention will become apparent upon consideration of the following detailed disclosure of the invention, especially when it is taken in conjunction with the above figures.

#### Description of The Preferred Embodiments

The membrane used to divide the electrolytic cell into anolyte and catholyte compartments is an oxidation-resistant, cation-permeable ion exchange membrane. Appropriate sealing means, such as gaskets or an O-ring, are used to create a liquid-tight seal between the membrane and the cell frame.

A suitable cathode is an electrode made of smooth, perforated stainless steel. The cathode is positioned in the cathode cell frame between the cathode backing mesh and the mesh spacer which separate the cathode and the cation-permeable ion exchange membrane. The preferred structure of the cathode is a smooth, perforated stainless steel of grades such as 304, 316, 310, and the like. The perforations should be large enough to permit release of hydrogen bubbles from between the membrane and the cathode. Other suitable cathode materials include nickel or nickel-chrome based alloys. Titanium or other valve metal cathode structures can also be used. A corrosion resistant alloy is preferred to reduce formation of some localized iron corrosion by products on the cathode surface due to potential chlorine dioxide diffusion through the membrane by surface contact with the cathode. Other suitable materials for the cathode include fine woven wire structures on an open type metal substrate, which can help to reduce the cell voltage by promoting hydrogen gas bubble disengagement from the surface of the cathode.

Multiple cathode conductor posts transmit electrical current from a power supply (not shown) through current splitter wire and cathode conductor post nuts to the cathode. Cathode conductor post fittings extend into the cathode frame about posts to seal against posts and prevent the leakage of catholyte from the cell.

The anode side of the cell contains a porous, high surface area anode and an anode backplate or current distributor fitted within the compartment. The anode is an electrode made of a porous and high surface area material. The high surface area material increases the rate of mass transport into and away from the surface of the anode and distributes the current so that the rate of charge transfer from the electrode to the anolyte solution is much lower than the rate of charge transfer through the membrane and the electrolyte. Materials with a surface area to volume ratio of about  $50 \text{ cm}^2/\text{cm}^3$  or higher are suitable for achieving a high percentage conversion of chlorite to chlorine dioxide. Higher surface area to volume ratios are more desirable up to the point where the pressure drop becomes critical. The anode must be sufficiently porous to permit the anolyte to pass through it during operation. The porosity must also be sufficient so that the effective ionic conductivity of

the solution inside the electrode is not substantially reduced. Anodes with a void fraction of greater than about 40% are suitable to accomplish this.

Preferred high surface area porous anodes are disclosed in U.S. 5,294,319 (issued March 15, 1994 to Kaczur et al.). A thin deposited platinum conductive coating or layer on a corrosion resistant high surface area ceramic, or a high surface, a titanium fiber structure, or a plastic fiber substrate can also be used.

Multiple anode conductor posts transmit electrical current from a power supply (not shown) through current splitter wire and anode conductor post nuts to the anode. Anode conductor post fittings extend into the anode frame about posts to seal against posts and prevent the leakage of anolyte from the cell.

The anolyte current distributor or backplate distributes the current evenly to the flexible and compressible porous, high surface area anode which does most of the high efficiency electrochemical conversion of the chlorite solution to chlorine dioxide.

A porous high surface area material of a compressible graphite felt or cloth construction can be used as the anode. The graphite surfaces can be impregnated with metallic films or metallic oxides to increase the life of the graphite. Other alternatives include fluoride surface-treated graphite structures which are used to improve the anodes useful life by preventing degradation due to the generation of small amounts of by-product oxygen on the surface of the graphite. Since such graphite structures are relatively inexpensive, they can be used as disposable anodes that can be easily replaced after a finite period of operation.

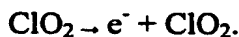
The anode backplate or current distributor can be similarly made of a graphite material which can be surface-treated with agents such as those used on the porous, high surface area anode material. Other alternative materials suitable for use in the current distributor include metallic films or metallic oxides on stable, oxidation-resistant valve metal structures such as titanium, tantalum, niobium, or zirconium. The coatings include metallic platinum, gold, or palladium coatings, or other precious metal coatings or oxide coatings.

A suitably diluted alkali metal chlorite feed solution, preferably sodium or potassium chlorite, is fed into anolyte compartment through the anode feed inlet and anolyte solution distributor channels at a suitable flowrate to allow for the electrochemical conversion of the chlorite ion to chlorine dioxide by the flexible or rigid compressible, porous, high oxygen over voltage, high surface area anode. The electrical current is conducted to the high surface area anode by the high oxygen over voltage anode backplate or current distributor which has one or more metallic anode conductor posts to conduct the DC electrical power from a DC power supply (not shown). Fittings are used to seal against conductor posts to prevent solution leakage from the cell. Current splitter

wire and anode conductor post nuts are used to distribute the electrical current to the anode distributor. The resulting chlorine dioxide solution or chlorine dioxide mist (anolyte effluent) exits through the anode outlet.

Softened, deionized, or demineralized water is educted into the catholyte inlet port and catholyte distribution orifices into the catholyte compartment at a flowrate sufficient to maintain a suitable operating concentration of alkali metal hydroxide in the catholyte. The alkali metal hydroxide is formed by alkali ions (not shown) passing from the anolyte compartment through the cation permeable ion exchange membrane into catholyte compartment and by the electrical current applied at the cathode to form the hydroxyl ions (OH<sup>-</sup>) at the cathode surface. The reaction at the cathode produces hydrogen gas, as well as hydroxyl ions, from the electrolysis of water. The catholyte alkali metal hydroxide solution by-product and hydrogen gas (not shown) pass through the cathode compartment into the catholyte outlet for removal from the cell under vacuum through the catholyte effluent tubing catholyte eductor check valve and into the catholyte eductor.

Electrolysis occurs in the cell as the chlorite solution passes parallel to the membrane through the anolyte compartment, causing the chlorine dioxide concentration to increase in the anolyte compartment as the chlorite ion concentration decreases according to the following reaction at the anode:



Alkali metal ions, for example, sodium (Na<sup>+</sup>), from the anolyte pass through the membrane. As the chlorite ion content of the anolyte decreases and the chlorine dioxide content increases, a portion of the chlorine dioxide can be oxidized at the anode, depending upon the pH, to the undesirable chlorate according to the following reaction:



This undesirable reaction can be avoided by maintaining a suitably acidic anolyte, and especially at higher pH's, by controlling the potential at the anode surface while providing mass transport of the chlorite ions from the bulk solution to the anode surface and transport of chlorine dioxide away from the anode surface. This permits high chlorine dioxide yields to be obtained.

The gaskets are preferably made of an oxidation-resistant rubber or a plastic elastomeric material. Suitable gaskets are those made from rubber-like materials such as ethylene vinyl acetate (EVA) or ethylene-propylene-diene monomer (EPDM) or gaskets sold under the trademark Viton<sup>®</sup>, and the like. Other suitable gasket materials include flexible closed foam types made from polyethylene, or polypropylene, or EVA which can be easily compressed to a thin layer to minimize distances between the membrane and the anode and cathode structures.



Oxidation and high temperature resistant membranes are preferred. Among these are perfluorinated sulfonic acid type membranes such as DuPont NAFION<sup>®</sup> types 117, 417, 423, 450 and the like, membranes such as those disclosed in U.S. Pat. No. 4,470,888, and other polytetrafluorethylene-based membranes with sulfonic acid groups such as those sold under the RAIPORE tradename by RAI Research Corporation. types of membranes that are membranes having combinations of sulfonic acid/carboxylic acid moieties, including those sold under the ACIPLEX tradename by the Asahi Chemical Company and under the FLEMION<sup>®</sup> trademark by the Asahi Glass Company.

A non-blinding thin mesh spacer can also be used between the cathode and the membrane. The spacer used in the catholyte compartment should also be a non-conductive plastic with large enough holes for ease of disengagement of the hydrogen gas from the catholyte compartment. The generator preferably is operated with the membrane of the cell in contact with the non-blinding plastic spacer and the spacer material when they are employed and with the membrane in contact with the cathode electrode and the anode electrode when they are not employed.

The preferred anolyte feed solution is sodium chlorite with a feed concentration of about 0.1 to about 30 g/L for one-pass through flow operation.

Additives in the form of salts, such as alkali metal phosphates, sulfates, chlorides and the like, can be used in the chlorite feed solution to increase the conversion efficiency, to reduce operating voltage, to provide pH buffering of the final product solution or mist, or add to stabilize the chlorine dioxide solution during storage.

In operation, the cell operates with the electrolytes at a temperature of from about 5° C to about 50° C, with the preferred operating temperature being about 10° C to about 30° C. The preferred method of introducing the anolyte feed, e.g., buffered sodium chlorite solution, is to dilute it in line in the generator, by mixing with softened or deionized water to the desired concentration before the anolyte feed enters the anolyte compartment. (see Figure 7) An alternative would be to pre-dilute the anolyte feed solution (undiluted sodium chlorite) separately from the electrochemical generator by using an eductor which is designed to automatically draw in the undiluted sodium chlorite under vacuum and dilute it to the users desired concentration. This prediluted solution can then be used as a single anolyte feed to the electrochemical cell without the need for additional dilution and/or preparation. The catholyte is either deionized water or softened water, depending on what is readily available and depending on whether the by-product sodium hydroxide has a potential end use in other areas of the installation, e.g., for controlling pH.

The cell uses an operating current density of from about 0.01 KA/m<sup>2</sup> to about 10 KA/m<sup>2</sup>, with the preferred range being about 0.05 KA/m<sup>2</sup> to about 3 KA/m<sup>2</sup>. The constant operating cell

voltage and electrical resistance of the anolyte and catholyte solutions are limitations of the operating cell current density that must be traded off or balanced with current efficiency and conversion of chlorite to chlorine dioxide. The cell operating voltage depends on the oxygen over voltage of the anode materials used in the anode structures. The higher the oxygen over voltage of the anode materials, the higher the voltage at which the generator can be operated and still maintain a high current efficiency and yield chlorine dioxide. The typical operating voltage range is between about 2.0 to about 7.0 volts, with a preferred range being about 2.5 to about 4.0 volts.

Additionally, the ratio of the total surface area of the anode to the superficial surface area or projected area of the membrane impacts the current density at which the generator can be operated and the total generator voltage. The higher that this particular ratio is, the greater is the maximum current density, and the lower is the total generator voltage, at which the generator can be operated.

The anolyte flow rate through the cell and the residence time of the anolyte in the cell are factors that affect the conversion efficiency of chlorite to chlorine dioxide. There are optimum flow rates to achieve high efficiency conversion and to obtain the specific pH final product solution or mist needed for the commercial applications for a single pass flow through system. The typical pH range is about 2.5 to about 8.0. Typical residence times for the single pass flow through system in the cell to achieve high conversion of chlorite to chlorine dioxide with high current efficiency are between about 0.1 to about 10 minutes, with a more preferred range being about 0.5 to about 4 minutes. Very long residence times can increase chlorate formation as well as reduce the pH of the product solution to very low values (i.e., pH 2 or below) which may be detrimental to the anode structures.

The catholyte and by-product sodium hydroxide concentration should be about 0.1 to about 30% weight, preferably about 0.5 to about 10 weight %. The optimum hydroxide concentration will depend on the membrane's performance characteristics. The higher the caustic or sodium hydroxide concentration, the lower is the calcium concentration or water hardness needed for long life operation of the membrane.

The amount of gaseous chlorine dioxide in the mist is from about 0.0001% to less than 10% by volume. The amount of chlorine dioxide in the aqueous solution is from about 0.01 to about 8 grams per liter.

#### Analytical Test Methods For Determining Chlorine Dioxide Concentration and Conversion

The sample to be tested is obtained by placing a flexible hose to the sample port's barbed fitting, running this hose to the bottom of the amber sample bottle, and slowly and completely filling the bottle with anolyte effluent from the generator. The bottle should be capped and the

analysis should be immediately carried out using a chlorine dioxide specific Dreager apparatus for the mist containing the gaseous chlorine dioxide or a photometric detector for the mist containing the gaseous chlorine dioxide or the chlorine dioxide solution.

#### Free Oxidants

The free oxidants are determined by placing ~100 mls of deionized (D.I.) water into an erlenmeyer flask and adding Potassium Iodide Powder Pillow (#1077-99), adding 1 ml of pH 7 Buffer, Phosphate Type (#21553-32), then adding 1-2 ml (V) of generator effluent beneath the surface of the D.I. water using a 0.113N (N) Sodium Thiosulfate Titration Cartridge (#22673-01) and a digital titrator, add the titrant until the solution turns a straw yellow color, then add a few drops of starch solution (#349-32) before titrating the solution to a colorless endpoint.

$$A = \frac{(\text{digits}/800)}{V \text{ (mls)}}$$

#### Total Oxidants

The total oxidants are determined by adding to the above sample one Dissolved Oxygen Powder Pillow (#987-99), allowing the reaction to take place in the dark for 5 minutes, and titrating to a colorless endpoint using a 0.113N (N) Sodium Thiosulfate Titration Cartridge (#22673-01) and a digital titrator. Add the titrant until the solution turns a straw yellow color, then add a few drops of starch solution (#349-32) before titrating the solution to a colorless endpoint.

$$B = \frac{(\text{digits}/800)}{V \text{ (mls)}}$$

#### Unsparged Chlorine

The unsparged chlorine is determined by placing ~100 mls of D.I. water into an erlenmeyer flask, adding 1 ml of pH 7 Buffer, Phosphate Type (#21553-32), and then adding 1-2 ml (V) of anolyte effluent from the generator beneath the surface of the water. The solution is sparged for 15 minutes using a gas dispersion tube and an inert gas (either nitrogen or helium), and then adding one Potassium Iodide Powder Pillow (#1077-99). Using a 0.113N (N) Sodium Thiosulfate Titration Cartridge (#22673-01) and digital titrator and the titrant until the solution turns a straw yellow color, then add a few drops of starch solution (#349-32) before titrating to a colorless endpoint.

$$C = \frac{(\text{digits}/800)}{V \text{ (mls)}}$$

Unreacted Chlorite

The unreacted chlorite is determined by adding to the above sample one Dissolved Oxygen Powder Pillow (#987-99). The mixture is allowed to react in the dark for 5 minutes. Using a 0.113N (N) Sodium Thiosulfate Titration Cartridge (#22673-01) and digital titrator, add the titrant until the solution turns a straw yellow color, then add a few drops of starch solution (#349-32) before titrating to a colorless endpoint.

$$D = \frac{(\text{digits}/800)}{V \text{ (mls)}}$$

All of the reagents necessary to carry out the above tests are available from Hach, Inc. P.O. Box 389, Loveland, CO 80539-9986. The following calculations are used to determine the parts per million (ppm) of chlorite ( $\text{ClO}_2$ ), chlorine dioxide ( $\text{ClO}_2$ ), and chlorine ( $\text{Cl}_2$ ), the efficiency, i.e., conversion, and excess chlorine ( $\text{Cl}_2$ ).

$$\begin{aligned} \text{ppm ClO}_2 &= 5/4 \times (B - D) \times N \times 13,490 \\ \text{ppm ClO}_2 &= D \times N \times 16,863 \\ \text{ppm Cl}_2 &= [A - (B - D)/4] \times N \times 35,450 \\ \text{Efficiency} &= \frac{\text{ClO}_2 \times 100\%}{\text{ClO}_2 + \text{ClO}_2} \\ \text{Excess Cl}_2 &= \frac{\text{Cl}_2/35.45 \times 100\%}{[(\text{ClO}_2 + \text{ClO}_2)/67.45]} \end{aligned}$$

In order to exemplify the results achieved, the following examples are provided without intent to limit the scope of the present invention to the discussion therein.

Example 1

An Oxychlor e™ (Trademark of International Dioxide, Inc.) chlorine dioxide generator was tested by feeding a diluted solution of sodium chlorite (2%) buffered at about pH 9 with a sodium carbonate/bicarbonate to the anolyte compartment. While the anolyte solution was educted through the anode compartment of the electrolytic cell softened water was pumped through the cathode compartment of the electrolytic cell. This is also the case for subsequent examples 2, 3, and 4 below. The cell described in the preceding figures has support ribbings for the membrane.

The results are shown below in Table 1.

Table 1

<u>Power</u>		<u>Anolyte</u>		<u>Catholyte</u>		<u>Conversion</u>		
<u>Volts</u>	<u>Amps</u>	<u>gpd</u>	<u>Vacuum</u> ( <u>psig</u> )	<u>gpd</u>	<u>Pressure</u> ( <u>psig</u> )	<u>pH</u>	<u>ClO<sub>2</sub></u> <u>Titration</u> s	(%)
4.31	80	65	10.3	85	3	3.0	A = 95 B = 625	72
4.35	83	65	10.3	85	3	4.5	A = 89 B = 761	53
4.29	81	65	7.4	85	3	3.0	A = 76 B = 498	72

The added membrane support ribbing on the anode side of the electrolytic cell significantly improved the conversion, as shown by the comparative data shown in Tables 2, 3, 4, and 5 below. The same generator was used but the electrolytic cell contained no support strips for the membrane.

Table 2

<u>Power</u>		<u>Anolyte</u>		<u>Catholyte</u>		<u>Conversion</u>		
<u>Volts</u>	<u>Amps</u>	<u>gpd</u>	<u>Vacuum</u> (psig)	<u>gpd</u>	<u>Pressure</u> (psig)	<u>pH</u>	<u>ClO<sub>2</sub></u> <u>Titration</u> s	<u>(%)</u>
4.39	97.5	57 <sup>a</sup>	10.8	85	3	3.1	A = 38 B = 506	32.5
4.44	97.5	57 <sup>a</sup>	10.8	85	3	3.3	A = 56 B = 638	38.5
4.43	97.5	58 <sup>a</sup>	10.8	85	3	3.5	A = 46 B = 650	30.5
4.38	82	65 <sup>b</sup>	10.3	85	3	3	A = 46 B = 552	36
4.37	80	65 <sup>b</sup>	10.3	85	3	3.28	A = 43 B = 535	35
4.32	77.5	65 <sup>b</sup>	10.3	85	3	3.5	A = 42 B = 541	33.7
3.87	67.5	50.5 <sup>c</sup>	10.3	65	3	3	A = 38 B = 438	38
3.89	66	50.5 <sup>c</sup>	10.3	65	3	3.25	A = 33 B = 402	35.8
3.87	65	50.5 <sup>c</sup>	10.3	65	3	3.5	A = 39 B = 480	35.4
4.53	110	50.5 <sup>c</sup>	10.3	65	3	2	A = 35 B = 405	38

a. 80% of design capacity

b. 90% of design capacity

c. 70% of design capacity

Without the anode supports, the conversions were consistently low even at varying production levels (e.g., 80%, 90% and 70% of design capacity). The low conversion was believed to be due to differential pressure across the Nafion membrane which deflected the membrane toward the anode. The resulting channeled flow probably reduces the residence time, resulting in poor conversion.

#### Example 2

Using the electrolytic generator of Example 1 with support ribbing for the cell's membrane, additional runs were carried out where the pH of the anolyte effluent varied. The results are shown in Table 3 below.

Table 3

<u>Power</u>		<u>Anolyte</u>		<u>Catholyte</u>		<u>Conversion</u>		
<u>Volts</u>	<u>Amps</u>	<u>gpd</u>	<u>Vacuum</u> (psig)	<u>gpd</u>	<u>Pressure</u> (psig)	<u>pH</u>	<u>ClO<sub>2</sub></u> <u>Titration</u> s	(%)
5.68	120	65 <sup>a</sup>	6.4	106	3	3	A = 137 B = 930	69.1
5.5	97.5	65 <sup>a</sup>	6.4	106	3	3.75	A = 52 B = 365	66.7
6.24	97.5	65 <sup>a</sup>	6.4	106	3	4.5	A = 38 B = 333	51

a. 90% of design capacity

At the 90% of design capacity level the conversion decreased as the pH of the chlorine dioxide level increased.

#### Example 3

Using the electrolytic generator of Example 1 with the supported ribbing for the cell's membrane, an additional run was carried out at 30% of design capacity. The results are shown in Table 4 below.

Table 4

<u>Power</u>		<u>Anolyte</u>		<u>Catholyte</u>		<u>Conversion</u>		
<u>Volts</u>	<u>Amps</u>	<u>gpd</u>	<u>Vacuum</u> (psig)	<u>gpd</u>	<u>Pressure</u> (psig)	<u>pH</u>	<u>ClO<sub>2</sub></u> <u>Titration</u> s	(%)
4.73	50	22 <sup>a</sup>	7.1	85	3	3	A = 34 B = 272	57

a. 30% of design capacity

The results show that at pH 3 and 30% of design capacity the conversion was only 57%, whereas at pH 3 and 90% of design capacity the conversion was 69.1% (see Table 3).

#### Example 4

Using the electrolytic generator of Example 3 with additional support ribbings for the cell's membrane (see Figure 5), an additional run was carried out at 90% and 30% of design capacities. The results are shown in Table 5.

Table 5

<u>Power</u>		<u>Anolyte</u>		<u>Catholyte</u>		<u>Conversion</u>		
<u>Volts</u>	<u>Amps</u>	<u>gpd</u>	<u>Vacuum</u> (psig)	<u>gpd</u>	<u>Pressure</u> (psig)	<u>pH</u>	<u>ClO<sub>2</sub></u> <u>Titration</u>	(%)
5.2	96.5	65 <sup>a</sup>	6.4	106	3	2.7	A = 78 B = 520	71
5.2	96.5	65 <sup>a</sup>	6.4	106	3	2.8	A = 112 B = 776	68
5.2	96.5	65 <sup>a</sup>	6.4	106	3	5.2	A = 45 B = 334	63
5.2	96.5	22 <sup>b</sup>	6.4	106	3	2.4	A = 185 B = 151	53

a. 90% of design capacity

b. 30% of design capacity

Similar to the previous example, at comparable pH values, operation at 90% of design capacity results in an improvement in yield over operation at the 30% of design capacity level. In either case, there was a notable improvement in yield with the use of the membrane support ribbing.

Example 5

With the same electrolytic cell used in Example 4, the electrolytic generator was modified such that both the anolyte and catholyte feed were educted through the cell under vacuum. The results of this trial are outlined below in Table 6.

Table 6

	1	1 Duplication	2	3	4	5	6	7
Voltage	6.3	6.3	6.7	6.64	6.85	4.66	5.28	5.56
Amperes / #ClO <sub>2</sub>	11	11	12.8	12.8	14	12	14	16
pH of Anolyte	7.44	7.44	6.9	6.75	3	7.6	6.7	1.9
Free ClO <sub>2</sub>	372	352	362	401	359	290	269	242
% Conversion to Free ClO <sub>2</sub> *	62	63	67	73	75	68	75	77

\* based on 100% of design capacity

Example 6

This example describes the production of a mist containing gaseous chlorine dioxide, air, and water vapor. The mist is useful as a dry disinfectant for products such as fresh produce, grains,



tobacco, and clay. It can also be used to disinfect fields, greenhouses, storage cellars, and autoclaves.

Chlorine dioxide mist is generated using the generator shown in Figure 1A. The electrolytic cell is the same as the cell used in the previous example. The eductor used should have a #6 nozzle with a 0.089 inch orifice diameter. The eductor motive gas pressure should be 10 psig and the back gas pressure should be 6 psig. The motive gas is air flowing at a rate of 3 SCFM (standard cubic feet per minute). The feed rate of the buffered aqueous sodium chlorite solution (Anthium Dioxide®) should be 39.6 lb/hr. The gas flow from the electrolytic cell should be 0.15 CFM and the gas production rate should be 2 lb/hr. The concentration of chlorine dioxide gas in the (mist should be about 5% by volume

Now that the preferred embodiments of the invention have been described in detail, various modifications and improvements thereon will become readily apparent to those skilled in the art. Accordingly, the spirit and scope of the present invention are to be limited only by the appended claims and not by the above specification.

**WHAT IS CLAIMED IS:**

1. An electrolytic generator, operated under a vacuum, for producing a solution of chlorine dioxide in one pass by the electrolysis of an anolyte which is a buffered aqueous alkali metal chlorite solution, which generator comprises in combination:
  - (a) a high surface area, porous anode with multiple electrode posts;
  - (b) a corrosion-resistant, highly conductive cathode with multiple electrode posts;
  - (c) a cation ion exchange membrane which separates the anode and the cathode and forms an anolyte compartment and a catholyte compartment;
  - (d) an array of non-corrosive support ribbings for the cation exchange membrane;
  - (e) a non-blinding mesh spacer between the cation exchange membrane and the cathode;
  - (f) catholyte and anolyte cell frames with inlet ports to the catholyte and anolyte compartments at the bottom of the cell frames, with outlet ports from the catholyte and anolyte compartments at the top of the cell frames, and with internal flow distribution headers enclosing the anolyte and catholyte compartments;
  - (g) an anolyte infeed means for introducing the buffered aqueous alkali metal chlorite anolyte into the anolyte compartment, which infeed includes a line with a solenoid followed by a rotameter and a flow switch;
  - (h) an inlet means for softened, deionized, or demineralized purge water, which means includes a line with a solenoid followed by a rotameter and a flow switch, which means is connected to the anolyte infeed line by a juncture and a line leading from the juncture to the anolyte inlet port;.
  - (i) a catholyte infeed means for introducing softened, deionized, or demineralized water to the catholyte port, which means includes a line with a solenoid followed by a rotameter and a flow switch;
  - (j) an ascending anolyte outfeed means, connected to the cell frame at the top on the anolyte side, to remove the aqueous chlorine dioxide anolyte effluent from the anolyte outlet port;
  - (k) an eductor connected to the anolyte outfeed means for creating a vacuum in the anolyte compartment by which the anolyte is drawn through the anolyte compartment;
  - (l) a motive water infeed means for supplying water to the eductor;

(m) a catholyte outfeed means, connected to the catholyte outlet port, to remove the alkaline hydroxide catholyte effluent containing entrained hydrogen, which means has a non-corrosive check valve before the eductor;

(n) a sensor, connected to the anolyte outfeed means prior to the eductor, for monitoring the anolyte effluent;

(o) a pressure switch on the motive water infeed means; and

(p) a DC power supply and an automatic current interrupter to prevent reverse current flow across the cell upon shutdown.

2. An electrolytic generator, operated under a vacuum, for producing a mist of gaseous chlorine dioxide, inert gas, and water vapor in one pass by the electrolysis of an anolyte which is a buffered aqueous alkali metal chlorite solution, which generator comprises in combination:

(a) a high surface area, porous anode with multiple electrode posts;

(b) a corrosion-resistant, highly conductive cathode with multiple electrode posts;

(c) a cation ion exchange membrane which separates the anode and the cathode and forms an anolyte compartment and a catholyte compartment;

(d) an array of non-corrosive support ribbings for the cation exchange membrane;

(e) a non-blinding mesh spacer between the cation exchange membrane and the cathode;

(f) catholyte and anolyte cell frames with inlet ports to the catholyte and anolyte compartments at the bottom of the cell frames, with outlet ports from the catholyte and anolyte compartments at the top of the cell frames, and with internal flow distribution headers enclosing the anolyte and catholyte compartments;

(g) an anolyte infeed means for introducing the buffered aqueous alkali metal chlorite anolyte into the anolyte compartment, which infeed includes a line with a solenoid followed by a rotameter and a flow switch;

(h) an inlet means for softened, deionized, or demineralized purge water, which means includes a line with a solenoid followed by a rotameter and a flow switch, which means is connected to the anolyte infeed line by a juncture and a line leading from the juncture to the anolyte inlet port;.

(i) a catholyte infeed means for introducing softened, deionized, or demineralized water to the catholyte port, which means includes a line with a solenoid followed by a rotameter and a flow switch;

(j) an ascending anolyte outfeed means, connected to the cell frame at the top on the anolyte side, to remove the chlorine dioxide-containing anolyte effluent from the anolyte outlet port;

(k) an eductor connected to the anolyte outfeed means for creating a vacuum in the anolyte compartment by which the anolyte is drawn through the anolyte compartment;

(l) a gas infeed means for supplying an inert gas to the eductor;

(m) a catholyte outfeed means, connected to the catholyte outlet port, to remove the alkaline hydroxide catholyte effluent containing entrained hydrogen, which means has a non-corrosive check valve before the eductor;

(n) a sensor, connected to the anolyte outfeed means prior to the eductor, for monitoring the anolyte effluent;

(o) a pressure analyzing means on the gas infeed means;

(p) a DC power supply and an automatic current interrupter to prevent reverse current flow across the cell upon shutdown;

(q) a pressure relief means on the anolyte outfeed means;

(r) a temperature analyzing means on the anolyte outfeed means;

(s) a pressure means on the anolyte outfeed means;

(t) a gas flow means on the anolyte outfeed means;

(u) an analyzing means for determining the amount of chlorine dioxide gas present in the anolyte; and

(v) a back pressure valve on the anolyte outfeed means.

3. The generator of Claim 2, wherein the inert gas is air, carbon dioxide, helium, oxygen, or nitrogen.
4. The generator of Claim 3, wherein the inert gas is air.
5. The generator of Claim 1 or 2, further comprising a dilution water infeed means, for introducing into the anolyte infeed line softened, deionized, or demineralized water and a juncture joining the dilution water infeed means and anolyte infeed means;
6. The generator of Claim 3, further comprising an eductor connected to the catholyte outfeed line for creating a vacuum in the catholyte compartment; and an eductor connected to the dilution water infeed means for creating a vacuum to draw the catholyte effluent into the dilution water infeed means.

7. The generator of Claim 5, wherein the non-corrosive check valves are plastic check valves, and wherein the catholyte outfeed means is ascending.
8. The generator of Claim 1, further comprising an on/off valve for the motive water.
9. The generator of Claim 2, further comprising an on/off valve for the inert gas.
10. The generator of Claim 1 or 2, wherein the catholyte and anolyte infeed lines and the catholyte and anolyte outfeed lines are plastic tubings.
11. The generator of Claim 1 or 2, further comprising an electrical panel containing a sensor, safety indicators, and operation controls.
12. The generator of Claim 11, wherein the sensor is a pH meter, a conductivity probe, an oxidation-reduction potential probe, an amperometric detector, or a colorimetric absorption indicator.
13. The generator of Claim 1 or 2, wherein the anode is a fine fibrous conductive substrate.
14. The generator of Claim 13, wherein the substrate is titanium, niobium, zirconium, tantalum, aluminum, tungsten, hafnium, mixtures thereof, or alloys thereof.
15. The generator of Claim 14, wherein the substrate is coated with an electrocatalyst selected from precious metals, the oxides of platinum group metals, mixtures thereof, and alloys thereof.
16. The generator of Claim 15, wherein the precious metal is platinum, silver, or gold and wherein the platinum group oxides are prepared from ruthenium, rhodium, palladium, iridium, or osmium.
17. The generator of Claim 1 or 2, wherein the anode is a segmented fibrous titanium coated with platinum and wherein the cathode is a perforated stainless steel plate.
18. The generator of Claim 1 or 2, wherein the anode is an unsegmented fibrous titanium coated with platinum and wherein the cathode is a perforated stainless steel plate.
19. The generator of Claim 1 or 2, wherein the anolyte feed, prior to dilution, is about 0.01% to about 31 % by weight of sodium chlorite buffered at about pH 9.0 and wherein the anolyte feed, after dilution with the softened, deionized, or demineralized water, is about 0.01 to about 10 % by weight of sodium chlorite.
20. The generator of Claim 2, further comprising a back pressure valve, located downstream of the eductor.
21. The generator of claim 2, further comprising a demister tank having a discharge line located at the bottom of the demister collection sump and connected to a drainage tank located.

22. The generator of Claim 20, further comprising a gas sparger, located in the demister trap prior to the line connecting the demister trap to the drainage tank.
23. The generator of Claim 2, further comprising a pressure relief means located on the demister trap.
24. The generator of Claim 23, wherein the pressure relief means is a rupture disk.
25. A disinfecting mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor.
26. The mist of Claim 25, wherein the amount of gaseous chlorine dioxide is about 0.0001 to less than 10% by volume, wherein the amount of the inert gas is about 90% to about 99.9% by volume, and wherein the water vapor is about 1 to about 20% by volume.
27. The mist of Claim 25, wherein the inert gas is selected from the group consisting of air, carbon dioxide, helium, nitrogen, and oxygen.
28. The mist of Claim 27, wherein the inert gas is air.
29. A method of disinfecting crops using the mist of Claim 25.
30. The method of Claim 29, wherein the crops are fresh produce, grains, or tobacco.
31. The method of Claim 30, wherein the produce includes vegetables and fruits.
32. A method of disinfecting clay using the mist of Claim 25.
33. A method of disinfecting fields, greenhouses, storage cellars, agricultural equipment, and ventilation equipment using the mist of Claim 25.
34. A method of disinfecting porous surfaces using the mist of Claim 25.
35. The method of Claim 34, wherein the porous surface is wood or concrete.
36. An electrolytic process for preparing a mist consisting essentially of gaseous chlorine dioxide, an inert gas, and water vapor, which process comprises the steps of:
  - (a) feeding a buffered aqueous alkali metal chlorite solution into the anolyte compartment of an electrolytic generator;
  - (b) feeding water into the catholyte compartment of the electrolytic generator;
  - (c) supplying a motive inert gas to an eductor to create a vacuum in the anolyte compartment; and
  - (d) and recovering the mist from the anolyte compartment.
37. The method of Claim 36, further comprising the steps of supplying a motive inert gas to an eductor to create a vacuum in the catholyte compartment.

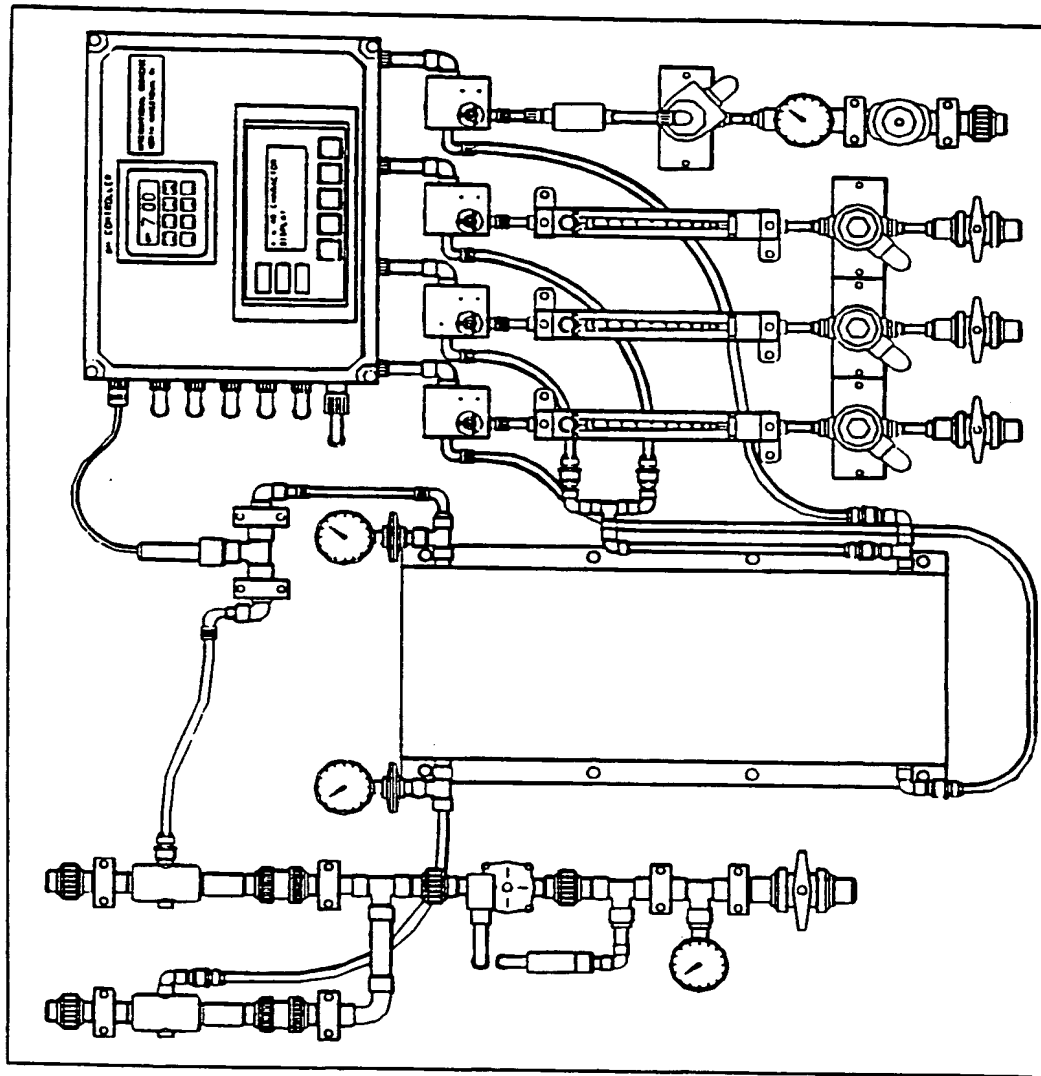


FIG.1

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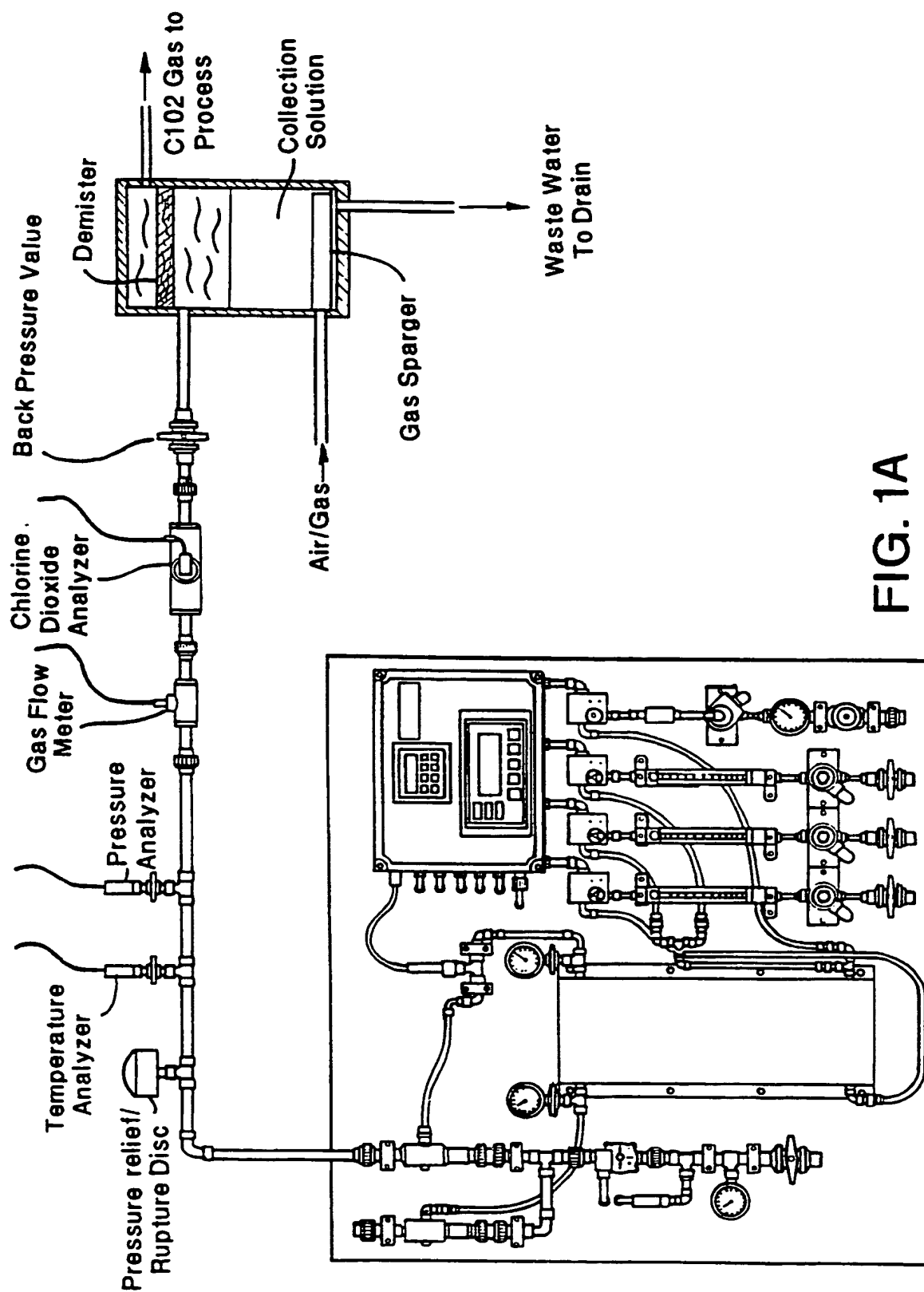
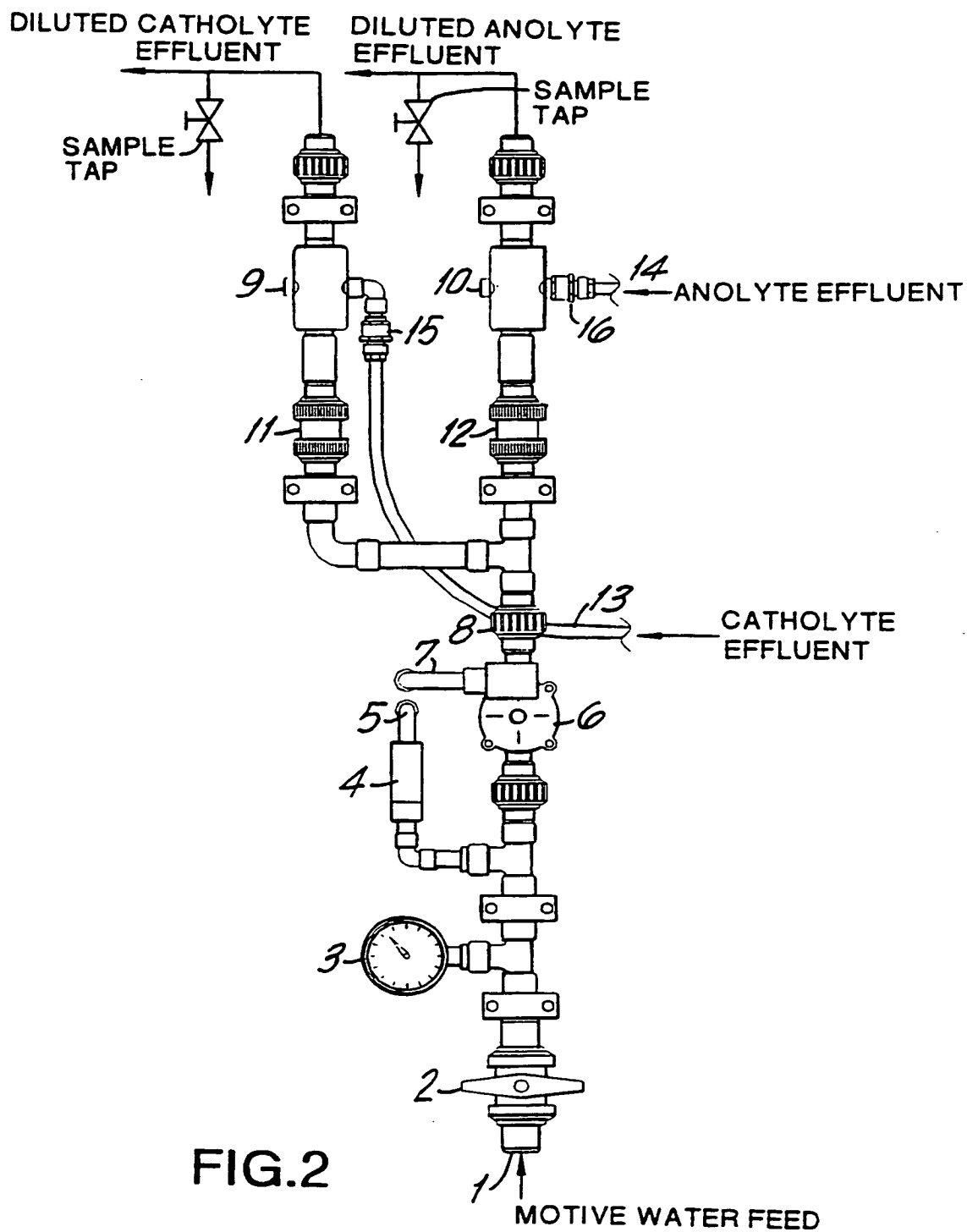


FIG. 1A



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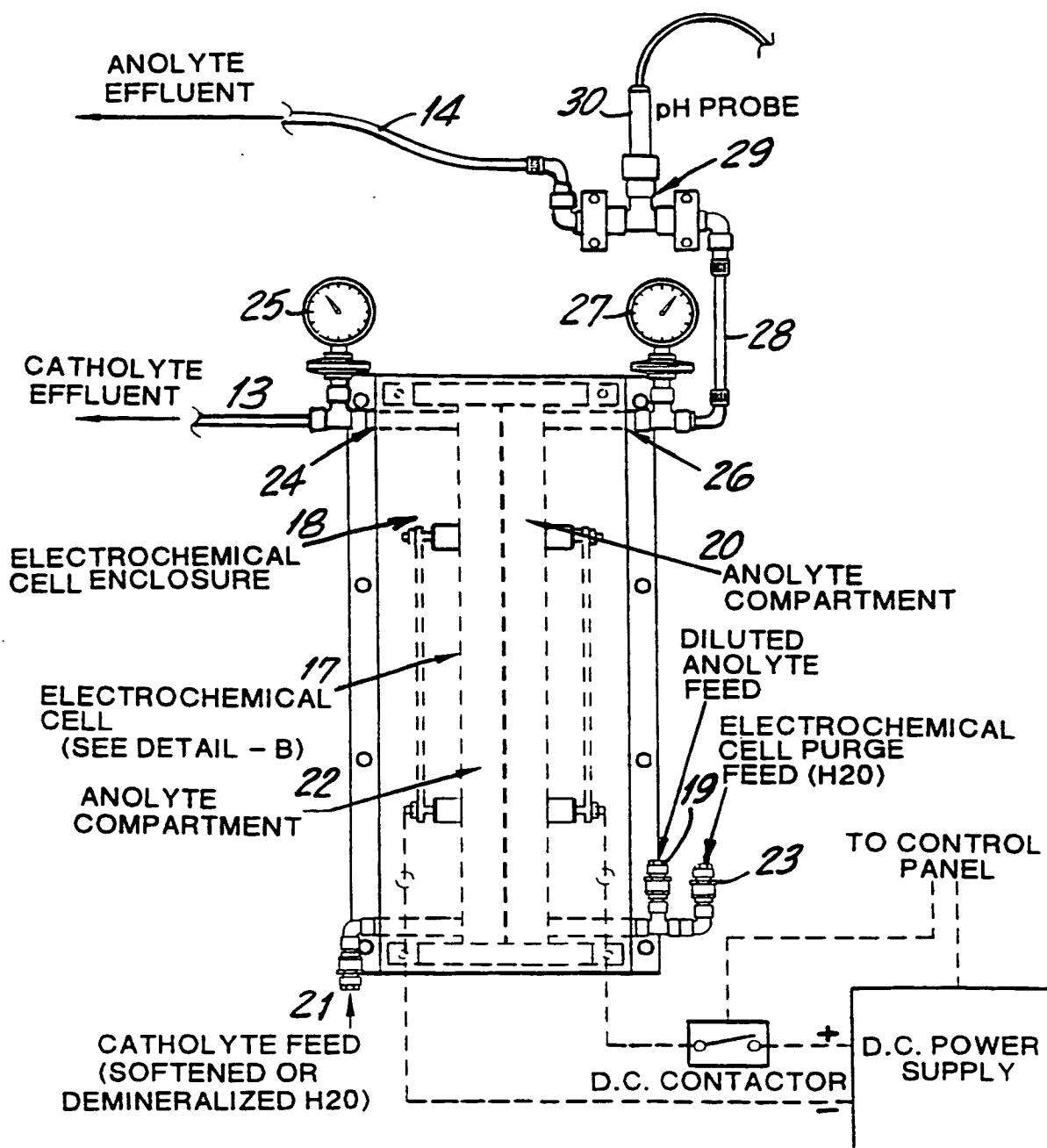


FIG.3

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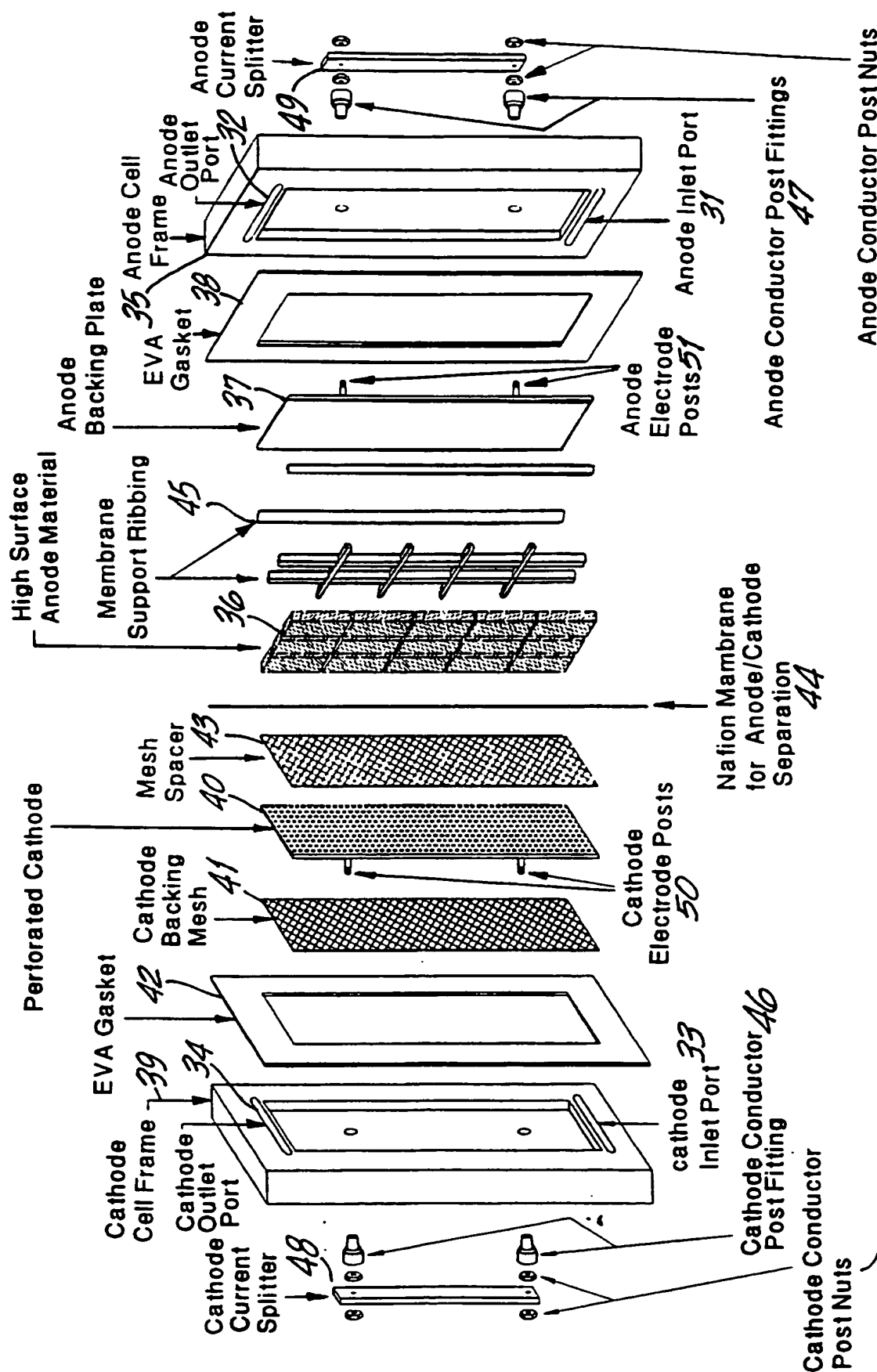
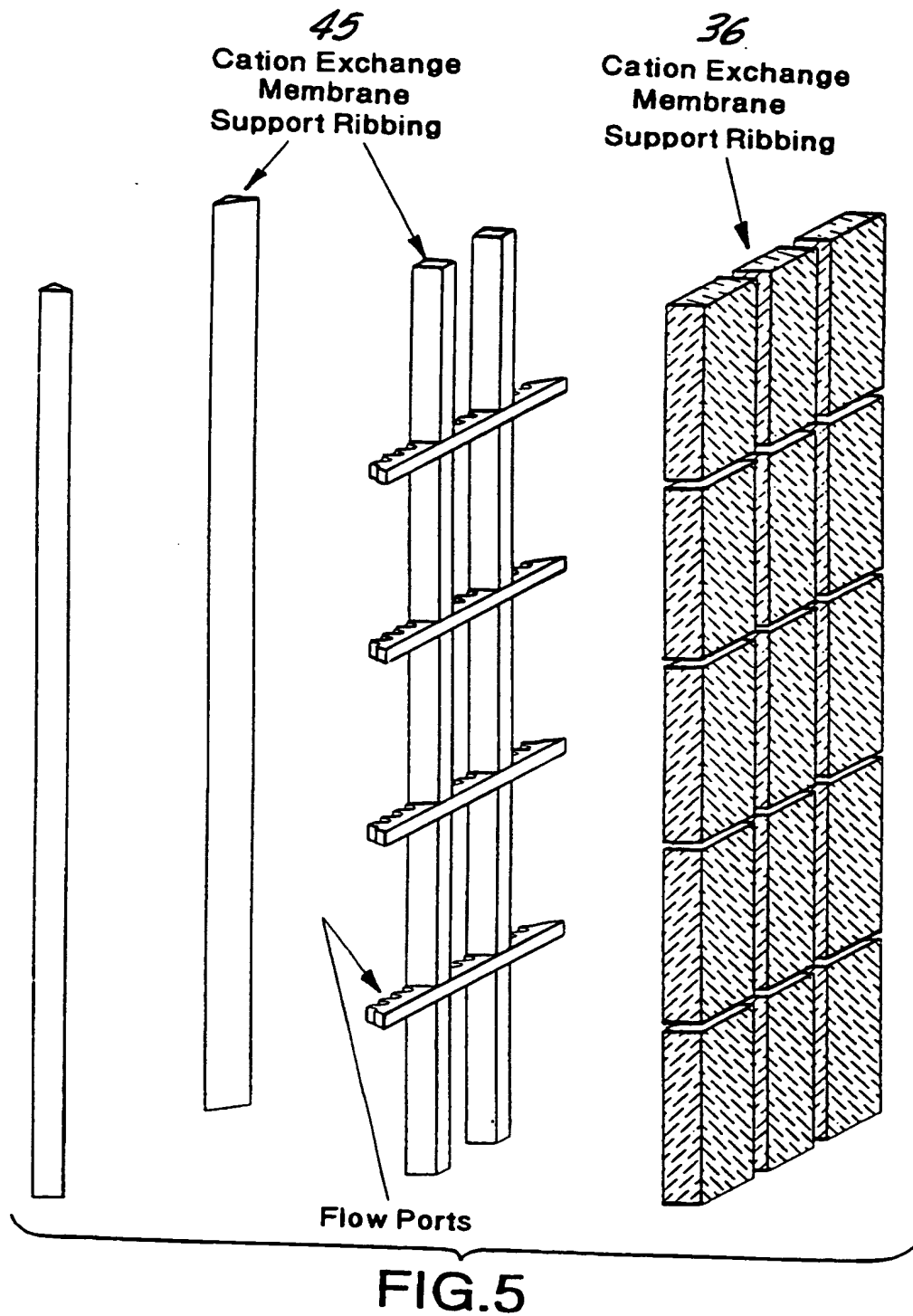


FIG.4



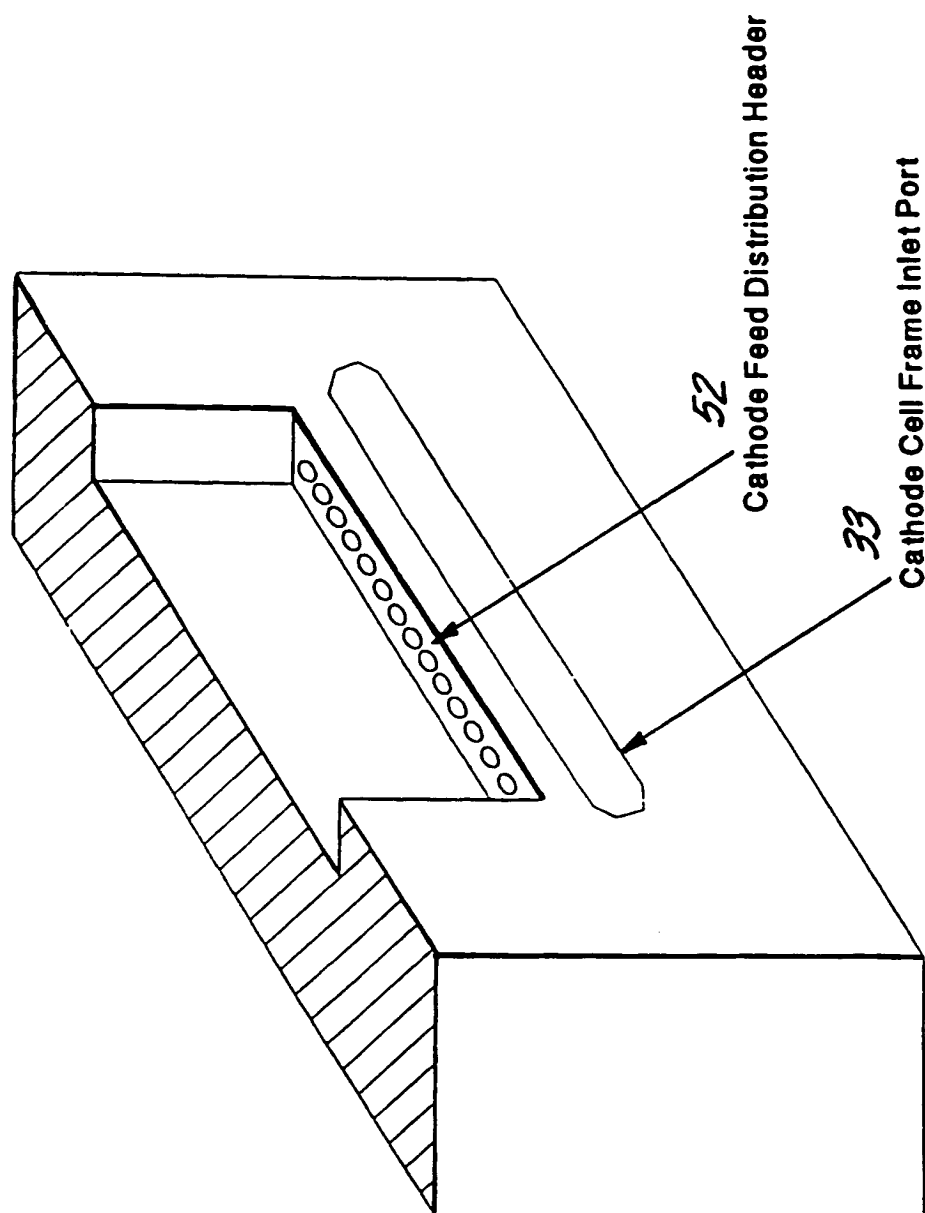


FIG. 6

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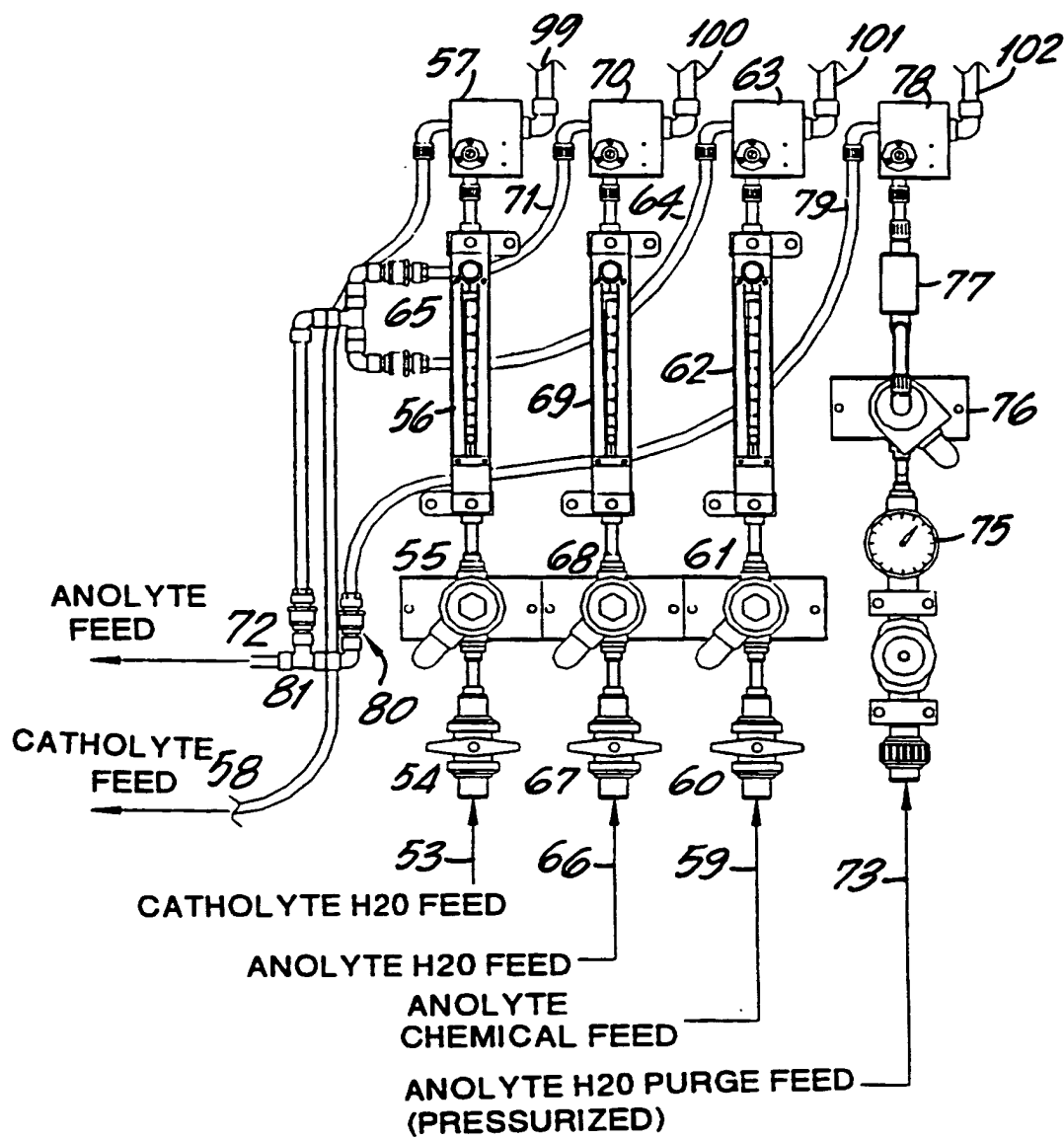


FIG. 7

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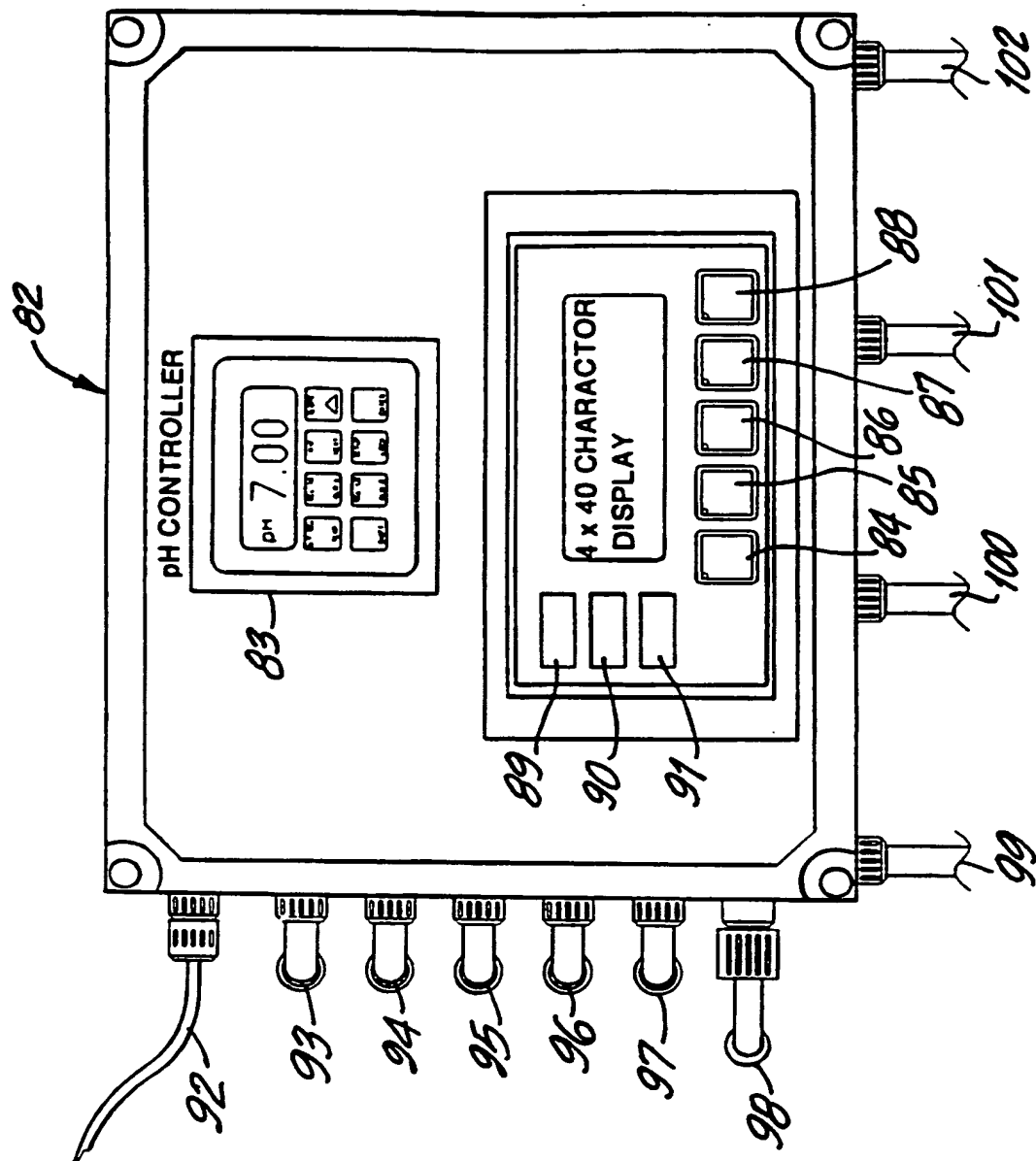


FIG. 8

# INTERNATIONAL SEARCH REPORT

Application No

PCT/US 00/23911

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C25B1/26 A61L9/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C25B A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 158 658 A (DAVID W. CAWLFIELD) 27 October 1992 (1992-10-27) cited in the application column 15 -column 16; claims 1-20 figures 1-3	1
A	US 4 456 510 A (KATSUYUKI MURAKAMI) 26 June 1984 (1984-06-26) column 7, line 4 - line 23 column 9 -column 12; claims 1,14	1
X	US 5 342 601 A (DAVID W. CAWLFIELD) 30 August 1994 (1994-08-30) column 5, line 13 - line 27	25,27
P,X	US 5 989 497 A (ROLAND R. LABONTE) 23 November 1999 (1999-11-23) column 4 -column 6; claims 1-18	25,32-35

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

10 January 2001

Date of mailing of the international search report

17/01/2001

Name and mailing address of the ISA

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NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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Authorized officer

Groseiller, P



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 00/23911

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5158658	A	27-10-1992	NONE		
US 4456510	A	26-06-1984	JP	1234572 C	17-10-1984
			JP	56158883 A	07-12-1981
			JP	59006915 B	15-02-1984
			CA	1184873 A	02-04-1985
			DE	3118795 A	11-03-1982
			US	4432856 A	21-02-1984
US 5342601	A	30-08-1994	US	5165911 A	24-11-1992
			AU	648929 B	05-05-1994
			AU	2199292 A	30-12-1992
			CA	2103245 A	18-11-1992
			DE	69216643 D	20-02-1997
			DE	69216643 T	15-05-1997
			DK	646095 T	07-07-1997
			EP	0646095 A	05-04-1995
			FI	935070 A	16-11-1993
			GR	3022716 T	30-06-1997
			HU	65907 A, B	28-07-1994
			JP	6507876 T	08-09-1994
			KR	148248 B	17-08-1998
			RU	2104247 C	10-02-1998
			WO	9220618 A	26-11-1992
US 5989497	A	23-11-1999	NONE		

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>3041-022</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/US 00/ 23911</b>	International filing date (day/month/year) <b>01/09/2000</b>	(Earliest) Priority Date (day/month/year) <b>03/09/1999</b>
Applicant  <b>INTERNATIONAL DIOXIDE, INC. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/23911

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C25B1/26 A61L9/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C25B A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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			WO 9220618 A	26-11-1992
US 5989497	A	23-11-1999	NONE	